West Virginia Department of
Commerce, Labor & Environmental Resources
Air Pollution Control Commission

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MEMORANDUM

TO: Ms. Judy D. Cooper
Administrative Law Division
Secretary of State's Office

FROM: Mr. G. Dale Farley
Director, APCC

DATE: January 6, 1992

SUBJECT: 45CSR21 Reference Material

Per our conversation last week concerning providing the Secretary of State's office with copies of reference material cited in 45CSR21, enclosed are photocopies of non-copyrighted reference material for your 45CSR21 files.

A list of copyrighted material is also included in the enclosure. The material may be reviewed, upon request, at our Charleston office at 1558 Washington Street, East (Telephone: 304 348-0430).

GDF/JAB/skm

Enclosure

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Commerce, Labor & Environmental Resources
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Charleston, West Virginia 25311

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REFERENCE MATERIAL FOR 45CSR21 "REGULATIONS TO PREVENT AND CONTROL AIR POLLUTION FROM THE EMISSION OF VOLATILE ORGANIC COMPOUNDS"

Photocopies of Reference Material Provided to Secretary of State's Office

EPA-450/3-88-018
Protocol for Determining the Daily Volatile Organic Compound Emission Rate of Automobile and Light-Duty Truck Topcoat Operations - December 1988

EPA-450/2-78-051
Control of Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems

EPA-450/2-78-029 (Appendix B)
Control of Volatile Organic Compound Emissions from Manufacture of Synthesized Pharmaceutical Products

EPA-450/2-78-041
Measurement of Volatile Organic Compounds

EPA-340/1-86-016
A Guideline for Surface Coating Calculations

EPA-450/3-84-019 (Revised June 1986)
Procedures for Certifying Quantity of VOC Emitted by Paint, Ink, and Other Coatings

EPA-450/2-82-015
APTI Course SI 417 - Controlling VOC Emissions from Leaking Process Equipment

EPA-340/1-86-015
Portable Instrument User's Manual for Monitoring VOC Sources

EPA-450/3-88-010
Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP

EPA-340/1-80-008
Petroleum Refinery Enforcement Manual (Appropriate Excerpts)

EPA Traceability Protocol 1
Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors

Federal Register. October 26, 1989.
Appendix D: Performance Specifications for Continuous Emissions Monitoring of Total Hydrocarbons in Hazardous Waste Incinerators, Boilers and Industrial Furnaces. 54:206 pp. 43743-43745.

Copyrighted Reference Material.
May be Reviewed at WVAPCC Office
1558 Washington Street, East
Charleston, West Virginia

American Society of Testing & Materials (ASTM) - D2879
D2879-83
D396-78
D2880-78
D975-78
D323-72
E260
E168
E169
D86
D97-66
D322-80
D2504-67
D2382-76(77)
D1946-77
D3925
E300
D4457-85

American Petroleum Institute Bulletin 2517
Evaporation Loss from External Floating-Roof Tanks

EPA-450/3-88-018

Protocol for Determining the Daily Volatile Organic Compound Emission Rate of Automobile and Light-Duty Truck Topcoat Operations

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1988

This report has been reviewed by the Emission Standards Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Copies of this report are available through the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, or from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

PUBLICATION NO. EPA-450/3-88-018

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1 - INTRODUCTION

This protocol determines the daily VOC emission rate (pounds of VOC per gallon of coating solids deposited) for a complete automobile and light-duty truck topcoat operation. The protocol considers the following factors:

-Daily usage of each coating
-VOC generated per gallon of each coating used
-Volume solids content of each coating used
-Daily weighted transfer efficiency of each coating used
-Daily weighted bake oven exhaust control credit

The protocol describes how to determine each of these factors, including the necessary testing and recordkeeping.

The protocol is designed for use in cases where (1) the topcoat emission limit is stated in units of pounds of VOC per gallon of solids deposited, (2) compliance is to be demonstrated for each day, and (3) the entire topcoat operation (i.e., all spray booths, flash-off areas and bake ovens where topcoat is applied, dried, and cured; except final off-line repair) is treated as a single entity.

The protocol uses the number of square feet coated on each vehicle in each booth with each coating as the basis for the daily weighting of individual transfer efficiency and bake oven exhaust control values. These data are also used to prorate the total usage of each coating in a month to each of the production days in that month. This can be done in lieu of directly monitoring and recording the usage of each category each day. Therefore, the emission rate for each day in a month is calculated at the end of that month.

Sample information sheets and calculations are provided in Appendix A. Use of these sample sheets is not required by the protocol. Alternative data presentation formats may be chosen by the owner/operator. A schematic drawing of the sample coating line used in the examples is presented in Figure 1. Some notes on the sample coating line are presented in Figure 2.

The protocol is intended as a living document which will be improved as experience is gained with its use. The protocol is divided into small sections which are amenable to changes, addition of new sections and incorporation into computer programs. The equations are presented in a form that is amenable to incorporation into computer programs. In some equations, asterisks ("*") are used to indicate multiplication and slashes ("/") are used to indicate division. The protocol as presented here is complete and must be used in its current form for compliance determinations.

In using the protocol, the owner/operator must initially identify various test conditions and parameters, data collection procedures and data presentation formats. For example, the owner/operator needs to choose the spray booths and coatings for transfer efficiency test (Sections 18 and 19) and a method of accounting for coating withdrawals (Section 25). These choices are subject to review by the appropriate regulatory agency(ies). The owner/operator should therefore discuss these choices with the agency(ies) before tests are performed or data are collected. Pre-test review, which is a requirement of many regulations and permits, provides an opportunity to identify and resolve potential issues in advance and thereby minimize the chances of later questions about the representativeness or validity of data and the need for retesting or redesign of data collection procedures or data presentation formats.

The protocol was originally published on June 10, 1988. This printing includes changes and additions made in November and December of 1988. The changes and additions are summarized in Appendix B.

2 - DEFINITIONS

Formulation Solvent Content - The weight of photochemically reactive organic solvents in a specific volume of coating (pounds per gallon) as determined using the procedures in Sections 11, 31, and 32. Volatile by-products of cross-linking reactions (cure volatiles) are not included in the formulation solvent content.

Mix Tank - A coating reservoir which is connected to the circulating system which delivers coating to the coating application equipment. Coating and dilution solvent are added to the circulating system through a mix tank. If the circulating system is kept full, changes in the coating level in a mix tank provide useful information for determining the volume of coating used over a period of time. Totes are mix tanks when they are plugged directly into the circulating system.

VOC Generated - The amount of VOC released from an as applied coating under specific application conditions, including cure volatiles released from those coating solids which are cured in a bake oven, and recognizing that cure volatiles are not released from coatings solids which are not cured in a bake oven. (i.e. overspray coating solids)

3 - SYMBOLS

Variables

BRFRAC(M,N) - Fraction of the total square footage coated on day N that is coated in spray booth M and baked in oven M. These are the bottom row fractions in the daily vehicle coating summary for day N (decimal fraction)

BTE(I,M) - Transfer efficiency for coating I in booth M (decimal fraction)

CA(I,J) - Analytical VOC content of the batch of coating I used in addition J (pounds of VOC per gallon)

CDE(M) - Efficiency of control device which treats exhaust from bake oven M (decimal fraction)

CDL(I,M) - VOC loading from coating I to control device which treats exhaust from bake oven M (pounds of VOC per gallon of solids deposited)

CF(I,J) - Formulation solvent content of the batch of coating I used in addition J (pounds of solvent per gallon)

CFRAC(I,M,N) - Fraction of total square footage coated in booth M on day N that is coated with coating I. These are the fractions in the column for booth M coating summary for day N (decimal fraction)

CP(I) - Volume of coating I that is captured by the purge capture system in a single purge cycle.

DAYSQFT(I,N) - Total square footage coated with coating I on day N (square feet)

DCC(N) - Total bake oven exhaust control credit for day N (pounds of VOC per gallon of solids deposited)

DENS(I,J) - Density of the batch of coating I used in addition J (pounds per gallon)

DER(N) - Daily emission rate for the topcoat operation on day N (pounds of VOC per gallon of solids deposited)

DSD(N) - Total volume of solids deposited on day N (gallons)

DVG(N) - Total mass of VOC generated on day N (pounds)

DVOL (I,J,A) - Density of the volatiles in ingredient A of the batch of coating I used in addition J (pounds per gallon)

END(I) - Volume level of coating I in mix tank at end of month (gallons)

GDAY(I,N) - Volume of coating I used on day N (gallons)

GMON(I) - Volume of coating I used in the month (gallons)

MONSQFT(I) - Square footage coated with coating I in the month (square feet)

NPURGE(I,N) - Number of purge cycles of coating I on day N

PADD(I,J) - Volume of coating I added to mix tank in addition J (gallons)

RADD(I,K) - Volume of dilution solvent added to the mix tank for coating I in addition K (gallons)

RCA(I) - Analytical VOC content of coating I (pounds of VOC per gallon, as applied)

RCF(I) - Formulation solvent content of coating I (pounds of solvent per gallon as applied)

RCV(I,N) - VOC generated per gallon of coating I on day N (pounds of VOC per gallon, as applied)

RD(I,K) - Density of dilution solvent added to the mix tank for coating I in addition K (pounds per gallon)

RVS(I) - Formulation volume solids content of coating I, as applied (decimal fraction)

RFRAC(I,M,N) - Fraction of total square footage coated with coating I on day N that is coated in booth M. These are the fractions in the row for coating I in the daily vehicle coating summary for day N (decimal fraction)

START(I) - Volume level of coating I in mix tank at start of month (gallons)

TCDL(M,N) - VOC loading to control device which treats exhaust from bake oven M weighed for day N (pounds of VOC per gallon of solids deposited)

TCP(I,N) - Total volume of coating I which is captured by purge capture system on day N (gallons)

TE(I,N) - Transfer efficiency for coating I on day N (decimal fraction)

VFS (I,J,A) - Volume solids content of ingredient A added to the batch of coating I used in addition J (decimal fraction)

VOL (I,J,A) - Volume of ingredient A added to the batch of coating I used in addition J (gallons)

VS(I,J) - Formulation volume solids content of the batch of coating I used in addition J (decimal fraction)

WITH(I,P) - Volume of coating I removed from mix tank for coating I in withdrawal P (gallons)

WITHTOT(I) - Total volume of coating I removed from mix tank for coating I in the month (gallons)

WT (I,J,A) - Mass of ingredient A added to the batch of coating I used in addition J (pounds)

WTFRSV (I,J) - Formulation weight fraction solvent content of the batch of coating I used in addition J (decimal fraction)

WTNR (I,J,A) - Weight fraction water or exempt solvent in ingredient A added to the batch of coating I used in addition J (decimal fraction)

WTSOLV (I,J,A) - Weight fraction solvent content of ingredient A added to the batch of coating I used in addition J (decimal fraction)

WTVOL (I,J,A) - Weight fraction volatiles content of ingredient A added to the batch of coating I used in addition J (decimal fraction)

Indices, Counters, Limits

A	Ingredient index for formulation calculations
B	Number of ingredients in the formula for a coating
BC	Base Coat
CC	Clear Coat
I	Coating Index
J	Coating Addition Index
K	Dilution Solvent Addition Index
L(I)	Number of Additions of Coating I in Month
M	Booth or Oven Index
N	Day Index
P	Withdrawal Index
R(I)	Number of Additions of Dilution Solvent to Mix Tank for Coating I in Month
S(I)	Number of Withdrawals from Mix Tank for Coating I in Month
T	Number of Booths/Ovens in Topcoat Operation
V	Number of Coatings Used
W	Number of (Operating) Days in Month
Y	Month Index

4 - DAILY VOC EMISSION RATE CALCULATION

The daily VOC emission rate is calculated by dividing the total pounds of VOC generated that day by the total gallons of solids deposited that day and then subtracting that day's bake oven exhaust control credit.

On day N, the daily emission rate is:

DER(N) = [DVG(N) / DSD(N)] - DCC(N)

A sample calculation is presented in Figure 20.

5 - TOTAL DAILY VOC GENERATED

The total VOC generated each day is calculated by multiplying the volume of each coating used that day by the pounds of VOC generated per gallon of that coating and summing the results.

The VOC generated on day N is:

$$DVG(N) = \sum_{I=1}^{V} [GDAY(I,N) * RCV(I,N)]$$

A sample calculation is presented in Figure 16.

6 - TOTAL DAILY SOLIDS DEPOSITED

The total gallons of solids deposited each day is calculated by multiplying the volume of each coating used that day by its formulation volume solids content and by its daily transfer efficiency and summing the results

The solids deposited on day N are:

$$DSD(N) = \sum_{I=1}^{V} [GDAY(I,N) * RVS(I) * TE(I,N)]$$

A sample calculation is presented in Figure 17.

7 - TOTAL DAILY BAKE OVEN EXHAUST CONTROL CREDIT

The bake oven exhaust control credit is determined for each day by weighting together the individual bake oven control device VOC loading values for that day and the previously determined incinerator efficiencies. The daily weighting factors are the fractions of the total square footage coated that day that are coated in the spray booth associated with each bake oven. These weighting factors are the bottom row fractions in the daily vehicle coating summary.

The bake oven exhaust control credit on day N is:

$$DCC(N) = \sum_{M=1}^{T} [TCDL(M,N) * CDE(M) * BRFRAC(M,N)]$$

A sample calculation is presented in Figure 19.

8 - DAILY COATING USAGE

The volume of each coating used each day can be calculated by prorating the volume of that coating used in a month to each day in the month. The prorating factor is the ratio of the total square footage coated with that coating on the day to the total square footage coated with that coating in the month.

The volume of each coating used on day N is:

GDAY(I,N) = GMON(I) * DAYSQFT(I,N) / MONSQFT(I)

A sample calculation is presented in Figure 14.

If the owner/operator chooses to make an adjustment for captured purge coating, then TCP(I,N) should be subtracted from the above result.

The owner/operator may elect to determine the daily usage of a coating directly by measuring the start-of-day and end-of-day volume of the coating in its mix tank, additions of the coating or dilution solvent to the mix tank, and withdrawals of coating from the mix tank. The daily usage is equal to:

STARTDAY - ENDDAY + ADDITIONS - WITHDRAWALS

9 - DAILY CALCULATION OF VOC GENERATED PER GALLON OF EACH COATING USED

The amount of VOC generated per gallon of each coating used is calculated each day using the analytical VOC content of the as applied coating, formulation solvent content of the as applied coating and the daily transfer efficiency for that coating.

The amount of VOC generated per gallon of coating I used on day N is:

$$RCV(I,N) = RCF(I) * [1 - TE(I,N)] + RCA(I) * TE(I,N)$$

A sample calculation is presented in Figure 15.

10 - ANALYTICAL VOC CONTENT OF AS APPLIED COATING

The analytical VOC content of an as applied coating can be calculated from records on the additions of coating and dilution solvents to that coating's mix tanks during the month.

For each addition of coating, the following information is needed:

- Gallons of coating added
- Analytical VOC content by EPA Method 24 (pounds by VOC per gallon) of the production batch from which the addition was made

For each addition of dilution solvent, the following information is needed.

- Gallons added
- Density (pounds per gallon)

The owner/operator may elect to have the EPA Method 24 analysis performed by the coating supplier or manufacturer. The owner/operator may elect to have the dilution solvent density value provided by the solvent supplier or manufacturer. All other information should be available from the owner/operator records of additions of coating and dilution solvent to mix tanks. Sample records are presented in Figure 11.

At the option of the owner/operator, a fixed (maximum) analytical VOC content value can be used for each coating as long as the use of such values does not underpredict the emission rate of the topcoat operation.

The analytical VOC content of the as applied coating I (pounds of VOC per gallon of coating) is equal to:

$$RCA(I) = \frac{\sum_{J=1}^{L(I)} [PADD(I,J) * CA(I,J)] + \sum_{K=1}^{R(I)} [RADD(I,K) * RD(I,K)]}{\sum_{J=1}^{L(I)} PADD(I,J) + \sum_{K=1}^{R(I)} RADD(I,K)}$$

A sample calculation is presented in Figure 13.

For waterborne coatings, if the precision adjustment factors in Reference Method 24 are used by the enforcing agency, the resulting analytical VOC content should never be less than the formulation solvent content. If the adjusted analytical VOC content is less than the formulation solvent content, then the analytical VOC content should be set equal to the formulation solvent content. That is:

If CA(I,J) LESS THAN CF(I,J) THEN CA(I,J) = CF(I,J)

11 - FORMULATION SOLVENT CONTENT OF AN AS APPLIED COATING

The formulation solvent content of an as applied coating can be calculated from records on the additions of coating and dilution solvents to that coating's mix tanks during the month.

For each addition of coating, the following information is needed:

- Gallons of coating added
- Formulation solvent content (pounds of solvent per gallon) of the production batch from which the addition of as supplied coating was made.

For each addition of dilution solvent, the following information is needed:

- Gallons added
- Density (pounds per gallon)

The owner/operator should obtain formulation solvent content data for the as supplied coating from the coating supplier or manufacturer. These data should be generated using the procedures described in Sections 31 and 32. The owner/operator may elect to have the dilution solvent density value provided by the solvent supplier or manufacturer. All other information should be available from the owner/operator records of additions of coating and dilution solvent to mix tanks. Sample records are presented in Figure 11.

At the option of the owner/operator, a fixed (maximum) formulation solvent value can be used for each coating as long as the use of such values does not underpredict the emission rate of the topcoat operation.

The formulation solvent content of the as applied coating I (pounds of VOC per gallon of coating) is equal to:

$$RCF(I) = \frac{\sum_{J=1}^{L(I)} [PADD(I,J) * CF(I,J)] + \sum_{K=1}^{R(I)} [RADD(I,K) * RD(I,K)]}{\sum_{J=1}^{L(I)} PADD(I,J) + \sum_{K=1}^{R(I)} RADD(I,K)}$$

12 - FORMULATION VOLUME SOLIDS CONTENT OF AS APPLIED COATINGS

The formulation volume solids content of an as applied coating can be calculated from records on the addition of coating and dilution solvents to that coating's mix tanks during the month.

For each addition of coating, the following information is needed:

- Gallons of coating added
- Formulation volume solids content of the production batch from which the addition of as supplied coating was made.

For each addition of dilution solvent, the following information is needed:

- Gallons added

The owner/operator should obtain formulation volume solids content data for the as supplied coating from the coating supplier or manufacturer. These data should be generated using the procedure in Section 33. All other information should be available from the owner/operator records of additions of coating and dilution solvent to mix tanks. Sample records are presented in Figure 11.

At the option of the owner/operator, a fixed (minimum) formulation volume solids value can be used for each coating as long as the use of such values does not underpredict the emission rate of the topcoat operation.

The volume solids content of the as applied coating I is equal to:

$$RVS(I) = \frac{\sum_{J=1}^{L(I)} [PADD(I,J) * VS(I,J)]}{\sum_{J=1}^{L(I)} PADD(I,J) + \sum_{K=1}^{R(I)} RADD(I,K)}$$

13 - DAILY TRANSFER EFFICIENCY

For each coating transfer efficiency shall be determined each day by weighting together the previously determined individual booth transfer efficiencies for that coating. The individual booth transfer efficiencies are the values for individual booths [or groups (parallel and/or series) of booths] determined by the procedures in Sections 18, 19 and 20. The daily weighting factors for each coating are the fractions of the total square footage coated with that coating that day that are coated in each booth [or group of booths] in which that coating is used. These weighting factors are the coating row fractions in the daily vehicle coating summary. These weighting factors provide the relative amount of solids deposited in each booth. An example calculation is presented in Figure 10.

The daily transfer efficiency for each coating is calculated by the following equation.

$$TE(I,N) = \frac{1}{\sum_{M=1}^{T} [RFRAC(I,M) / BTE(I,M)]}$$

Note that since the weighting factors give the relative amount of solids deposited in each booth, dividing a weighting factor by the appropriate transfer efficiency tells the amount of solids sprayed.

14 - DAILY INDIVIDUAL BAKE OVEN CONTROL DEVICE VOC LOADING VALUES

Bake oven exhaust control device VOC loading values are determined each day for each bake oven which is vented to a VOC control device by weighting together the previously determined coating specific bake oven control device VOC loading values for each coating used in the spray booth(s) associated with that bake oven. The weighting factors are the fractions of the total square footage coated that day in the spray booth(s) associated with the bake oven that were coated with each coating used in that spray booth(s).

$$TCDL(M,N) = \sum_{I=1}^{V} [CDL(I,M) * CFRAC(I,M,N)]$$

A sample calculation is presented in Figure 18.

As an alternative, the source owner or operator may choose to set

$$TCDL(M,N) = \min_{I=1}^{V} CDL(I,M)$$

15 - MONTHLY VEHICLE COATING SUMMARY

For each month, calculate the total number of square feet coated with each coating. These values can be calculated by summing the daily totals from the daily vehicle coating summary for each day in the month. If the owner/operator elects in Section 16 to use equivalent vehicles instead of square feet, then equivalent vehicles should be used in this Section too.

$$MONSQFT(I) = \sum_{N=1}^{W} DAYSQFT(I,N)$$

A sample monthly vehicle coating summary is shown in Figure 5.

16 - DAILY VEHICLE COATING SUMMARY

The coatings used and the number of square feet coated with each coating in each spray booth are determined daily. The square foot figures are determined from the specifications for each type or style of vehicle coated.

For each day, the total square feet coated with each coating in each booth is calculated. The fraction of the total square feet coated in each booth that is done with each coating and the fraction of the total square feet coated with each coating that is done in each booth are also calculated each day. These two items are the coating column fractions (CFRAC) and coating row fractions (RFRAC) in the daily vehicle coating summary. The fraction of the total square feet coated each day that is done in each booth is also calculated. This is the bottom row fraction in the (BRFRAC) daily vehicle coating summary. A sample daily vehicle coating summary is shown in Figure 4.

The owner/operator may elect to substitute "equivalent vehicles", and appropriate documented fractions thereof, for square footage values. Equivalent vehicle means a typical vehicle selected as the basis for equating an increase or decrease in the fractional size of all other vehicles or portions of vehicles coated in a particular topcoat operation calculated to the nearest 0.01 vehicle. A sample equivalent vehicle calculation is presented in Figure 22.

The owner/operator may elect to set the daily number of square feet of in-line repair work done with each coating equal to 4 percent of total square footage (excluding in-line repair) coated with that coating on that day. A sample calculation is presented in Figure 23.

A sample of the information needed for each vehicle processed is provided in Figure 3. The owner/operator may elect to record this information or just use this information to create running daily totals for the daily vehicle coating summary.

17 - MONTHLY COATING USAGE

The monthly usage of each as applied coating can be determined from the start-of-month and end-of-month volume of that coating in its mix tank, records of additions of coating and dilution solvent to the mix tank, and records of withdrawals of coating from the mix tank.

The following equation can be used to determine the monthly usage of an as applied coating.

$$GMON(I) = START(I) - END(I) + \sum_{J=1}^{L(I)} PADD(I,J) + \sum_{K=1}^{R(I)} RADD(I,J)$$

$$\ldots - \sum_{P=1}^{S(I)} WITH(I,P)$$

A sample calculation is presented in Figure 12.

18 - TRANSFER EFFICIENCY TEST PROCEDURE - IN PLANT

Applicability

This procedure can be used to determine by in-plant testing the transfer efficiency with which specific coatings are applied in an automobile or light-duty truck topcoat operation. The transfer efficiency of color and clear coats applied in main color booth(s) must be determined with this method or with the pilot line test method described in Section 19. The choice of in-plant or pilot line test is made by the owner/operator. At the option of the owner/operator, the transfer efficiency of other coatings applied in main color booth(s) (e.g., blackout) and coatings applied in other booths (e.g., separate "interior" color booth, tutone or in-line repair) may be determined by this procedure, by the pilot line test procedure described in Section 19, or by the alternate procedure described in Section 20 (Alternate Transfer Efficiency Procedure for Untested Booths and/or Coatings). The results determined by this procedure, the pilot line test procedure described in Section 19, and the alternate procedure described in Section 20 are combined for each coating each day in the Daily Transfer Efficiency Values section (Section 13).

Scope

This procedure for transfer efficiency uses the measured weight of coating solids applied to vehicles or foiled vehicles in production facilities.

Transfer Efficiency Procedure

A. The owner/operator selects the spray booth(s) to be included in the test. A main color booth must be included in the test. Each identical parallel booth in the same assembly line need not be tested.

B. The owner/operator selects the coatings to be used in the test. This procedure can be run for each coating used, but it is not necessary to test every coating. The coatings may be grouped based on processing sequence. Only one coating need be tested from each group and the result used for all of the coatinys in that group. Some sample groupinys are straight shades, non-metallic basecoats, metallic basecoats, mica basecoats and clear coats. These sample groupings are not the only possible groupings. Others may be appropriate based on processing sequence (e.g., the processing sequence for metallic basecoats and mica basecoats may be the same or silver basecoat may be applied with only air spray while all other metallic basecoats are applied with air spray and electrostatic spray). The owner/operator must explain in the test report the groupings used and the rationale for choosing a particular coatiny from each group for testing. To simplify testing and more closely represent actual process conditions, basecoat and clear coat can be tested together at the owner/operator option as noted later in this procedure.

C. Select an area in the facility for the body weighing or foil weighing which has relatively constant temperature and minimal air movement.

D. Topcoat must be the only coating applied during the test. If the body is weighed, weight loss from all other materials must be accounted for in the initial test weight.

E. A minimum of two foiled or unfoiled vehicle bodies (or major subassemblies thereof) are to be weighed to determine weight of solids applied. The test is considered acceptable if each final weight gain result is within 10 percent of the average weight gain.

F. Identify and preweigh vehicle bodies or major subassemblies to be painted to the nearest 0.05 lb. If foil method is used preweigh all available foil and tape. After vehicle is foiled, reweigh all unused foil and tape to determine beginning weight of test foil and tape by difference.

G. Isolate selected paint material at each spray station by using an auxiliary paint system or paint pots. Alternatively, at the owner/operator option, coating usage may be measured from the main circulating system tanks.

H. At the owner/operator option, determination of the amount of material used during the test may be made by weight or volumetric measurement as follows:

Weight Measurement

1. Weigh the tank of reduced paint after all supply and return lines have been filled, to nearest 0.05 lb.

2. Connect the paint tank to the system and paint the test vehicles or targets.

3. Reweigh the tank to nearest 0.05 lb.

4. Determine weight of paint material used by subtracting final weight of tank from the initial weight of tank.

5. Obtain paint samples for weight solids determination.

6. The initial and final weighings of the paint tank must both be done with the tank pressurized or both be done with the tank not pressurized.

Volume Measurement

1. a. Verify diameter of paint tank.

   b. Determine level in paint circulating tank prior to test, to nearest 0.1 inch.

2. Paint the test vehicles or targets. (It is suggested that the number of units painted should be chosen to achieve approximately a 3" to 4" drop in a typical circulating tank.)

3. Determine the paint level after the test to the nearest 0.1 inch.

   Paint usage from a cylindrical tank is determined as follows:

$$\frac{\text{Gallons Paint Used}}{\text{job}} = \frac{\pi r^2 h}{231n} - \text{Volume occupied by all other equipment in the measured section of the tank.}$$

   231 = Cubic inches per gallon

   π = 3.1416

r = Radius of tank in inches

h = Drop of paint level in tank in inches

n = Number of vehicle bodies or major subassemblies painted to achieve the measured liquid level drop in circulating tank

4. Obtain paint samples for testing weight solids fraction and coating density.

J. Reweigh the painted test vehicles, foil or components to the nearest 0.05 lb after paint has cured, and cooled.

K. Determine the weight solids of the paint samples using ASTM-D 2369-86.

L. Determine the coating density using ASTM-D 1475 (lb/gallon).

M. The transfer efficiency is calculated by dividing the weight of paint solids applied to the vehicle or foil by the weight of paint solids used.

Calculation for Paint Usage by Weight

$$\text{Transfer Efficiency} = \frac{\text{average weight gain of target}}{(\text{average weight coating consumed per job}) \times (\text{weight fraction solids})^*}$$

Calculation for Paint Usage by Volume

$$\text{Transfer Efficiency} = \frac{\text{average weight gain of target}}{(\text{average gallons coating used per job}) \times (\text{density}) \times (\text{weight fraction solids})^*}$$

The test result for coating I in booth M is referred to in the section on Daily Transfer Efficiency as BTE(I,M).

* If more than one coating is sprayed on each test vehicle (e.g. basecoat and clear coat), then the denominator is the sum of all solids sprayed.

General Comments

At the owner/operator option, separate transfer efficiency values for BC and CC can be determined directly by coating at least two vehicles with BC only and at least two vehicles with BC/CC. The average weight gain per job for CC only can be determined by subtracting the average weight gain per job for BC only from the average weight gain per job for BC/CC.

Frequency of Certification

Transfer efficiency tests must be conducted for an initial compliance test. The owner/operator must review the operating conditions annually thereafter. The most recent test results remain valid as long as the owner/operator demonstrates that no significant changes have occurred in paint technology or processing. Significant product, processing, material or application equipment changes will necessitate reevaluation of the transfer efficiency of the operations which have been modified. Such complete reevaluation must be done as soon as practicable (not later than 180 days after start-up) after start-up and stabilization of the new product, process, material or application equipment. The results of this reevaluation (i.e., new transfer efficiency values) must be used retroactively to the start-up of the new product, process, material or application equipment. Reevaluation is not necessary for:

A. Model year product changes, unless there are significant changes in size and shape of the typical vehicle.

B. Processing and material changes such as new model year or special order colors of the same formula type, minor changes in line rate, minor changes in processing sequence, minor changes in equipment types, etc.

19 - TRANSFER EFFICIENCY TEST PROCEDURE - PILOT LINE

A - Applicability

This procedure can be used to determine by pilot line testing the transfer efficiency with which specific coatings are applied in an automobile or light-duty truck topcoat operation. The transfer efficiency of color and clear coats applied in main color booth(s) must be determined with this method or with the in plant test method described in Section 18. The choice of in-plant or pilot line test is made by the owner/operator. At the option of the owner/operator, the transfer efficiency of other coatings applied in main color booth(s) (e.g., blackout) and coatings applied in other booths (e.g., separate "interior" color booth, tutone or in-line repair) may be determined by this procedure, by the in-plant test procedure described in Section 18, or by the alternate procedure described in Section 20 (Alternate Transfer Efficiency Procedure for Untested Booths and/or Coatings). The results determined by this procedure, the in-plant test procedure described in Section 18, and the alternate procedure described in Section 20 are combined for each coating each day in the Daily Transfer Efficiency Values section (Section 13).

B - Scope

This procedure for transfer efficiency uses the measured weight of coating solids applied to vehicles or foiled vehicles in pilot line facilities. The production line process is simulated in the pilot line. The pilot line data are validated against production line data to verify that a credible simulation has been carried out. Once the pilot line data have been validated, the pilot TE results are adjusted to improve the correlation with production line data.

C - Selection of Spray Booth(s) and Coating(s) to be Tested

1. The owner/operator selects the production spray booth(s) to be simulated in the pilot line test. Each identical parallel booth in the same assembly line need not be simulated separately.

2. The owner/operator selects the coatings to be used in the test. This procedure can be run for each coating used, but it is not necessary to test every coating. The coatings may be grouped by the owner/operator based on processing sequence. Only one coating need be tested from each group and the result used for all of the coatings in that group. Some sample groupings are straight shades, non-metallic basecoats, metallic basecoats, mica basecoats and clear coats. These sample groupings are not the only possible groupings. Others may be appropriate based on processing sequence (e.g., the sequence for metallic basecoats and mica basecoats may be the same or silver basecoat may be applied with only air spray while all other metallic basecoats are applied with air spray and electrostatic spray). The owner/operator must explain in the test report the groupings used and the rationale for choosing a particular coating from each group for testing. To simplify testing and more closely represent actual process conditions, basecoat and clear coat can be

tested together at the owner/operator option as noted later in this procedure. The coatings used in the pilot test must be coatings that are used in the plant (i.e., same manufacturer, product code and solvent reduction conditions).

D - In-Plant Survey and Data Collection

1. The owner/operator conducts an in-plant survey of the spray booth(s) to be simulated in the test to determine the operating parameters.

The following parameters must be noted:

- Number of spray stations
- Type and number of spray guns at each spray station
- Portion of vehicle coated at each spray station

Additional parameters may be noted at the option of the owner/operator. These additional parameters could include any or all of the following: (Note: The more parameters that are noted in the plant and faithfully reproduced in the pilot line test, the greater the likelihood of the pilot line test producing acceptable results which pass the tests for data validity.)

°Fluid nozzles and tips
°Air pressures at the heel of guns
°Electrostatic voltage settings
°Reciprocator trigger points
°Fluid delivery rate per gun
°Open gun times
°Paint temperature
°Paint viscosity

°Analytical weight solids
°Fan width
°Dry film thickness
°Gun to target distance
°Resistivity of paint
°Line speed adjusted to plant specifications
°Traverse speed (strokes per minute for recips, cycles for bells)
°Contour bar for reciprocators should be designed for vehicle being sprayed
°Booth balance
°Booth downdraft (lfpm)
°Booth temperature
°Booth relative humidity
°Bell RPM
°Bell shaping air
°Bell and recip. angles
°Set zone pressure to those at the process of interest

The in-plant values for each parameter noted must be recorded and presented in the test report. In situations where the coating of interest is applied in two or more "identical" parallel booths, the noted parameters must be measured in at least two of these booths. The individual booth measurements and average measurement must be presented in the test report.

2. For each coating to be tested, the owner/operator determines the average weight of solids sprayed per vehicle in the production booth(s) to be simulated. This is to be done either by determining the average mass of coating used per vehicle and multiplying by the analytical weight solids content, or by determining the average volume of coating used per vehicle and multiplying by the analytical coating density and by the analytical weight solids content.

The average mass or volume of coating used per vehicle may be determined from usage on a block of vehicles as in the in-plant TE test, from direct measurements (e.g., use of temporary in-line meters), or from gun on times and fluid flow rates. (See Parts L-7 and L-8 of this section.) In situations where the coating of interest is applied in two or more "identical" parallel booths, coating usage per vehicle must be determined using data from at least two of these booths.

3. For each coating to be tested, the owner/operator determines the average in-plant dry film build for Class I and Class II areas. This is to be done by taking before and after dry film build measurements on at least two vehicles. (See Part L-6 of this section). At least one before and after dry film build measurement must be made for each square foot of Class I surface area coated per vehicle. These measurements must be uniformly distributed over the Class I area of the vehicle, with the same distribution used for before and after measurements. At least two before and after dry film build measurements must be made for each square foot of Class II surface area coated per vehicle. [Large flat interior panels (e.g., interior of commercial panel vans) may be treated as Class I area for dry film build measurements.] These measurements must be uniformly distributed over the Class II area of the vehicle, with the same distribution used for before and after measurements. (See Part L-5 of this section.) In situations where the coating of interest is applied in two or more "identical" parallel booths, the vehicles on which the film build measurements are made must be coated in at least two of these booths.

4. The owner/operator calculates the overall average dry film build by weighting together the average Class I and Class II film builds by the square feet of Class I and Class II area coated per vehicle.

E - Pilot Line Set-Up

1. Select an area in the pilot facility for the body weighing or foil weighing which has relatively constant temperature and minimal air movement.

2. Topcoat must be the only coating applied during the test. If the body is weighed, weight loss from all other materials must be accounted for in the initial test weight.

3. Prepare the pilot line to simulate the in-plant conditions. The pilot line must use the same number of spray stations or steps as there are in-plant. At each station the same type and number of gun(s) must be used and the same portions of the vehicle must be coated. Additional parameters, documented in-plant are set in the pilot. The pilot line values for each parameter that was documented in-plant must be recorded and presented in the test report. Portions of the vehicle which are not designated for coating in-plant must not be coated to a greater extent in the pilot facility than they are coated in-plant (i.e., overspray that unavoidably lands in these areas in plant is acceptable in pilot, but intentional excess coating of undesignated areas in the pilot test is not acceptable).

F - Pilot Line Test

1. A minimum of two foiled or unfoiled vehicle bodies (or major subassemblies thereof) are to be weighed to determine weight of solids applied. The test is considered potentially acceptable, subject to pilot line data validation, if each final weight gain result is within 10 percent of the average weight gain.

2. Identify and preweigh vehicle bodies or major subassemblies to be painted to the nearest 0.05 lb. If foil method is used preweigh all available foil and tape. After vehicle is foiled, reweigh all unused foil and tape to determine beginning weight of test foil and tape by difference.

3. Isolate selected paint material at each spray station by using an auxiliary paint system or paint pots. Alternatively, at the owner/operator option, coating usage may be measured from the main circulating system tanks.

4. At the owner/operator option, determination of the amount of material used during the test may be made by weight or volumetric measurement as follows:

Weight Measurement

i. Weigh the tank of reduced paint after all supply and return lines have been filled, to nearest 0.05 lb.

ii. Connect the paint tank to the system and paint the test vehicles or targets.

iii. Reweigh the tank to nearest 0.05 lb.

iv. Determine weight of paint material used by subtracting final weight of tank from the initial weight of tank.

v. Obtain paint samples for weight solids determination.

vi. The initial and final weighings of the paint tank must both be done with the tank pressurized or both be done with the tank not pressurized.

Volume Measurement

i. a. Verify diameter of paint tank.

b. Determine level in paint circulating tank prior to test, to nearest 0.1 inch.

ii. Paint the test vehicles or targets. (It is suggested that the number of units painted should be chosen to achieve approximately a 3" to 4" drop in a typical circulating tank.)

iii. Determine the paint level after the test to the nearest 0.1 inch.

Paint usage from a cylindrical tank is determined as follows:

$$\frac{\text{Gallons Paint Used}}{\text{job}} = \frac{\pi r^2 h}{231n} - \text{Volume occupied by all other equipment in the measured section of the tank.}$$

231 = Cubic inches per gallon

π = 3.1416

r = Radius of tank in inches

h = Drop of paint level in tank in inches

n = Number of vehicle bodies or major subassemblies painted to achieve the measured liquid level drop in circulating tank

iv. Obtain paint samples for testing weight solids fraction and coating density.

5. Reweigh the painted test vehicles, foil or components to the nearest 0.05 lb after paint has cured, and cooled.

6. Determine the weight solids of the paint samples using ASTM-D 2369-86.

7. Determine the coating density using ASTM-D 1475 (lb/gallon).

8. For each coating tested, determine the average weight of solids sprayed per vehicle in the pilot test. This is done either by multiplying the average mass of coating used per vehicle by the analytical weight solids content, or by multiplying the average volume of coating used per vehicle by the analytical coating density and by the analytical weight solids content.

9. For each coating tested, the owner/operator determines the average pilot line dry film build for Class I and Class II areas. This is to be done by taking before and after dry film build measurements on at least two vehicles. (See Part L-6 of this section.) At least one before and after dry film measurement must be made for each square foot of Class I area coated per vehicle. At least two before and after dry film build measurements must be made for each square foot of Class II surface area coated per vehicle. The locations for film build measurements must be uniformly distributed over the Class I and Class II areas on vehicle with the same distribution used for before and after measurements. (See part L-5 of this section.)

10. The owner/operator calculates the overall average pilot line dry film build by weighting together the average Class I and Class II film builds by the square feet of Class I and Class II area coated per vehicle.

G - Pilot Line Data Validation

1. All of the following tests must be met (except as described in Part K) in order for the pilot data for a particular coating to be considered valid. If any of the following tests are not met, the pilot data are not valid and cannot be used to calculate in-plant transfer efficiency. (See Figure 24.)

2. The average weight of solids sprayed per vehicle in the pilot test must be within or equal to ± 20 percent of the average weight of solids sprayed per vehicle in-plant.

3. The overall average dry film build in the pilot test must be within or equal to ± 20 percent of the overall average dry film build in-plant.

4. The percent change in weight of solids sprayed per vehicle from plant to pilot and the percent change in overall dry film build from plant to pilot must be within 20 percentage points of each other.

$$\text{If } A = \frac{\text{Solids sprayed pilot - Solids sprayed plant}}{\text{Solids sprayed plant}} * 100$$

$$\text{and } B = \frac{\text{Overall film build pilot - Overall film build plant}}{\text{Overall film build plant}} * 100$$

then the absolute value of A - B must be less than or equal to 20.

H - Calculation of Pilot Line TE

1. If all the pilot line data validation tests are satisfied, then the pilot line TE is calculated by dividing the weight of paint solids applied to the vehicle or foil by the weight of paint solids used.

Calculation for Paint Usage by Weight (See Figure 25.)

$$\text{Pilot Transfer Efficiency} = \frac{\text{average weight gain of target}}{\text{(average weight coating consumed per job) x (weight fraction solids)*}}$$

Calculation for Paint Usage by Volume

$$\text{Pilot Transfer Efficiency} = \frac{\text{average weight gain of target}}{\text{(average gallons coating used per job) x (density) x (weight fraction solids)*}}$$

*If more than one coating is sprayed on each test vehicle (e.g., basecoat and clear coat), then the denominator is the sum of all solids sprayed.

I - Adjustment of Pilot Line TE

1. The pilot line TE values must be adjusted based on the differences in average weight solids sprayed per vehicle and overall average dry film build between the pilot line and the plant. (See Figure 26.) The adjusted values may be used in the section on Daily Transfer Efficiency. The adjusted pilot line test result for coating I in booth M is referred to as BTE(I,M).

$$BTE(I,M) = \text{Pilot TE} * \frac{\text{Solids sprayed pilot}}{\text{Solids sprayed plant}} * \frac{\text{Overall film build plant}}{\text{Overall film build pilot}}$$

J - Frequency of Certification

1. Transfer efficiency tests must be conducted for an initial compliance test. The owner/operator must review the operation conditions annually thereafter. Significant product, processing, material or application equipment changes will necessitate complete reevaluation of the transfer efficiency of the operations which have been modified. Such complete reevaluation must be done as soon as practicable (not later than 180 days after start-up) after start-up and stabilization of the new product, process, material or application equipment. The result of this reevaluation

(i.e., new transfer efficiency values) must be used retroactively to the start-up of the new product, process, material, or application equipment. Reevaluation is not automatically necessary for:

i. Model year product changes, unless there are significant changes in size and shape of the typical vehicle.

ii. Processing and material changes such as new model year or special order colors of the same formula type, minor changes in line rate, minor changes in processing sequence, minor changes in equipment types, etc.

2. If no significant changes occur over a year, the owner/operator must still revalidate and readjust the pilot test data annually. (See Figure 27.) This is done by conducting an annual in-plant survey of average weight of solids sprayed per vehicle and average Class I and Class II dry film build for each coating previously tested on the pilot line. (These data should be collected in the same manner as in the initial pre-test survey.) The pilot line test data are then revalidated against the new in-plant data as described in Parts G and K of this section. If all the required tests are passed, then the pilot data are still valid and new adjusted TE values are calculated as described in Parts I and K of this section. If the pilot data are no longer valid, then a new TE test must be conducted. (Note: If a coating that was used in the most recent pilot test is no longer used in-plant, then the annual revalidation and readjustment may be done using another coating from the same group of coatings.)

3. Similarly, at the owner/operator option, the effect of minor process or product changes on transfer efficiency may be taken into account at

any time without necessarily having to conduct a complete new pilot line test. This may be done by following the procedure in part J-2 of this section. If the pilot test data are still valid compared to the new in-plant data, then new adjusted TE values may be calculated without performing a new pilot TE test.

K - General Comments

At the owner/operator option, separate TE values for BC and CC can be determined directly by coating at least two vehicles with BC only and at least two vehicles with BC/CC. The average weight gain per job for CC alone can be determined by subtracting the average weight gain per job for BC only from the average weight gain per job for BC/CC.

The BC only vehicles and the BC/CC vehicles must meet the within 10 percent weight gain tests (Part F-1) for the test to be considered potentially valid, subject to pilot line data validation.

The BC/CC vehicles must pass all the pilot line data validation tests in Part G. The BC only vehicles must pass the test in Part G-2. The BC only vehicles do not have to be assessed with respect to the test in Part G-3, G-4 and G-5 (i.e., there is no need to collect BC only film build data in the plant).

The adjustments to pilot BC and pilot CC TE should be made as follows:

$$BTE(BC,M) = \text{Pilot BC TE} * \frac{\text{BC solids sprayed pilot}}{\text{BC solids sprayed plant}} * \frac{\text{Overall BC/CC film build plant}}{\text{Overall BC/CC film build pilot}}$$

$$BTE(CC,M) = \text{Pilot CC TE} * \frac{\text{CC solids sprayed pilot}}{\text{CC solids sprayed plant}} * \frac{\text{Overall BC/CC film build plant}}{\text{Overall BC/CC film build pilot}}$$

ADDED 11/88

L - Additional Information and Definitions

1. Each dry film build measurement should be performed consistent with ASTM B499-87, "Measurement of Coating Thicknesses by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals." The number of dry film build measurements should be as specified in parts D-3 and F-9 of this section, rather than as specified in part 6.3.4 of ASTM B499-87.

2. Class I means exterior surfaces designated to be coated that are visible with hood, deck lid and doors closed.

3. Class II means all surfaces designated to be coated that are not Class I.

4. All weight solids determinations must be done with ASTM D2369-86

5. Dry film build measurements are not required to be made on non-magnetic substrates (e.g., plastic parts) for which the magnetic instruments described in ASTM B499-87 cannot be directly used to measure coating thickness if the total designated coated area (Class I plus Class II) of these substrates is less than 25 percent of the total area (Class I plus Class II) coated on the vehicles. The total Class I and total Class II areas coated (including non-magnetic substrate area) must be used to determine the number of Class I and Class II dry film build measurements required and to calculate overall average dry film build. (See Figures 28 and 29.) The dry film build measurements that would normally be made on a particular part, but are not made because the part is constructed of a non-magnetic substrate must be made on a corresponding part. For example, if a vehicle has a 10 square foot Class I plastic front fender and no dry film build measurements are made on that fender, then the

(approximately) 10 measurements that would normally be made on the fender could be made as additional measurements on a rear quarter panel. Other examples of corresponding parts are hood and deck lid, engine compartment and trunk interior, etc.

If 25 percent, or more, of the total area (Class I plus Class II) coated on the vehicle is on non-magnetic substrates, then in-plant and pilot line dry film build measurement are required for the non-magnetic substrates. These measurements can be accomplished by wrapping the non-magnetic substrates with foil or by attaching magnetic basis metal (e.g., steel) shims to the non-magnetic substrates. The film build measurement device must be calibrated for the foil or shims.

6. The requirement to take before and after dry film build measurements on at least two vehicles can be met at the owner/operator option by taking before and after measurements on portions of a greater number of vehicles as long the equivalent of at least two complete vehicles (i.e., two of each panel or surface) is measured.

The before and after measurements for a particular panel or surface must be made on the same vehicle. An example of an equivalent vehicle would be all before and after measurements from front windshield forward on one vehicle, all before and after measurements from front windshield to rear windshield on a second vehicle, and all before and after measurements from the rear windshield back on a third vehicle. The equivalent vehicle approach may be helpful when the owner/operator chooses to perform in-plant dry film build measurements while the vehicles are still in process (e.g., on the conveyor) as opposed to removing the vehicles from the production line.

7. The method used to determine in-plant average mass or volume of coating used per vehicle is chosen by the owner/operator from the options presented in Part D-2 of this section. The in-plant determinations of average mass or volume of coating used per vehicle and Class I and Class II dry film builds must be made contemporaneously. For example, if coating usage per vehicle is determined from usage on a block of vehicles, then the vehicles on which film build measurements are made must be included in that block. If temporary in-line meters or fluid flow rates and gun on times are used to determine coating usage per vehicle for manual guns, the metering or gun on time measurements must include the manual coating of the vehicles on which film build measurements are made. If temporary in-line meters or fluid flow rates and gun on times are used to determine coating usage per vehicle for automatic guns, the metering or gun on time measurements must be done during the same shift in which the automatic coating of the vehicles on which film build measurements are made.

8. If gun on times and fluid flow rates are used to determine in-plant average coating usage per vehicle, caution must be used to account for fluid flow rate variation during the spray cycle of each piece of equipment. This variation could be caused by partial triggering of manual guns or fluid pressure changes in automatic guns.

20 - ALTERNATE TRANSFER EFFICIENCY PROCEDURES FOR UNTESTED BOOTHS AND/OR COATINGS

This section describes an alternate transfer efficiency procedure that may be used for those parts of the topcoat operation whose transfer efficiencies are not determined using the test procedure in either Section 19 or 20. These parts may include color and clear coatings applied in untested booths (e.g. separate "interior" color booth, tutone, or in-line repair); and other coatings applied in tested booths (e.g. blackout applied in a main color booth).

The following predetermined transfer efficiency values may be used by these situations:

Air Atomized Spray	40 percent
Electrostatic Spray	55 percent

If a particular coating is applied with both types of equipment, then the two transfer efficiency values should be weighted by relative square footage coated by each method.

$$\text{Transfer Efficiency} = \frac{1}{\frac{\text{Air Fraction}}{.4} + \frac{\text{Estatic Fraction}}{.55}}$$

Where Air Fraction + Estatic Fraction = 1

The transfer efficiency for coating I in booth M is referred to as BTE(I,M) in the section on Daily Transfer Efficiency.

21 - TEST PROCEDURE FOR DETERMINING BAKE OVEN EXHAUST CONTROL DEVICE VOC LOADING FOR SPECIFIC COATINGS

This procedure is used to determine the bake oven exhaust control device VOC loading for specific solvent-borne coatings used in an automobile or light-duty truck topcoat operation.

Scope

This procedure simulates the loss of VOC from a freshly painted surface by weight difference before and after baking. Metal test panels are subjected to simulated coating film build, flashing and baking sequence. The weight loss during baking is then related to the volume of solids deposited on the test panels to compute a control device inlet loading in pounds VOC per gallon solids applied. Identification of the points at which painted vehicles would enter oven zones whose effluents are vented to a control device provides the data needed to determine the oven VOC loading available for destruction in control device equipped zones.

A baking oven must be used to thoroughly cure the paint film. Gas-fired ovens are more representative of actual production; however, a vented electric oven may be used.

Film thickness is to be measured with an instrument, such as an Elcometer or Dualscope. Ensure that this equipment is capable of measurements on substrate selected if direct measurements on the panels are to be taken.

Process

The processing conditions must be determined prior to beginning the test, including film thicknesses, flash times, and baking sequence, to ensure use of values that represent the range of conditions found in the plant.

Identify all locations in the process sequence in which oven effluent is vented directly to a control device for VOC destruction. This will affect the number of panel weight measurements taken and the number of test panels that need to be run. If more than one oven is vented to a control device then panels need to be run for each different baking sequence and ventilation pattern.

Selection of Coatings for Evaluation

This procedure need not be run for each coating used. The coatings used may be grouped based on similar appearance characteristics, processing sequences and dry film thicknesses. One coating can be tested from each group and the result used for all of the coatings in that group. Some sample groupings are straight shades (colors that do not receive a clear coat), non-metallic basecoats, metallic basecoats, mica basecoats and clear coats. In order to more closely represent actual process conditions, basecoat and clear coat can be tested together at owner/operator option as noted later in the procedure.

For each coating evaluated, run triplicate test panels for each production bake oven which is vented to a control device.

Weight Measurements to be Recorded

Weigh panel before paint is applied (W)

Coat panel according to plant process sequence.

Weigh coated panel at point in bake cycle at which exhaust air is first vented to the incinerator (W1).

Weigh coated panel at point in bake cycle at which exhaust air is no longer vented to the incinerator (W2). (Note: Panel should be cooled to room temperature before weighing).

If W2 does not represent a fully cured coating film, then a duplicate painted panel should remain in the oven to complete the full bake cycle. Cool and weigh this panel (W3). [This weight (W3) should be used to determine the Gallons Solids Applied (GSA), covered later in this section].

Measurement of Film Thickness

Coupons should be coated and baked along with the test panels for measurement of film thicknesses of basecoat and clearcoat on the panels. For straight shade systems, film thickness measurements may be taken directly on the panels.

Dry film thickness measurements should be recorded for basecoat and clearcoat for each panel tested.

Determination of Dry Solids Density

Dry solids density may be calculated as shown below. Information needed to perform this calculation includes the weight fraction solids, volume fraction solids, and gallon weight of the coating materials as applied. These values should be determined using the procedures specified in EPA Method 24. The one-hour bake should be used in the weight fraction solids determination. The formulation volume fraction solids value should be generated using the procedure described in Section 33. Solids density is calculated using the following equation:

$$SD = \frac{WFS \times WGC}{VFS}$$

SD = Solids Density (lbs solids/gal solids)

WFS = Weight Fraction Solids (lbs solids/lbs paint)

WGC = Weight Per Gallon of Coating (lbs paint/gal paint)

VFS = Volume Fraction Solids (gal solids/gal paint)

If base coat and clear coat are applied to the same panel, determine the weighted average paint solids density by the ratio of film thickness as follows:

$$WSD = \frac{T1}{T1 + T2} \times D_{bc} + \frac{T2}{T1 + T2} \times D_{cc}$$

WSD = Weighed Solids Density

T1 = BC Film Thickness

T2 = CC Film Thickness

D_{bc} = BC Solids Density

D_{cc} = CC Solids Density

Calculations

The following calculations are used to express bake oven control device loading in pounds VOC per gallon solids applied (GSA).

Weight of coating solids applied = coated panel weight after full bake minus panel weight before coating application.

WPS = W3 - W or

WPS = W2 - W if W2 represents a fully cured paint film

where WPS = weight of coating solids applied

Weight of VOC available for control equals panel weight at point which all exhaust air is vented to control device minus panel weight at point which exhaust air is no longer vented to the control device.

WSA = W1 - W2

where WSA = weight of VOC available for control

Set up the following ratio for each panel measured:

weight of VOC available for control/weight of paint solids applied

RATIO = WSA/WPS

Convert this ratio to units of pounds VOC available for control per gallon of coating solids applied by multiplication of this ratio by paint solids density.

CDL = RATIO x WSD

where CDL = VOC loading expressed in terms of pounds VOC per gallon solids applied.

WSD = weighted solids density expressed in terms of pounds solids per gallon solids

Frequency of Certification

Bake oven exhaust control device VOC loading must be determined for an initial compliance test. The owner/operator must review the operating conditions annually thereafter. The most recent test results remain valid as long as the owner/operator demonstrates that no significant changes have occurred in coating technology or processing. A significant change in coating technology is considered to be a major difference in the generic nature of the coating chemistry. Annual variations in color palette or routine minor solvent blend adjustments for processing, quality, or other reasons do not constitute significant changes in coating technology. Significant process changes may include changing ducting to the incinerator, or major size modifications to spray booths, flash tunnels, or ovens.

Equipment

Use triplicate aluminum or thin steel panels with a minimum area of 20 square inches for each coating evaluated.

For weight measurements, use a balance with accuracy to 0.001g.

Coating is to be applied in a laboratory spray booth with booth air velocity representative of production conditions.

Coating materials must be the specific formulations (in as-applied condition) as used in the plant whose control device VOC loading is to be determined.

22 - BAKE OVEN EXHAUST CONTROL DEVICE EFFICIENCY

The efficiency of a bake oven exhaust control device (incinerator destruction efficiency) should be determined using the following methods for the inlet and outlet streams:

(a) EPA Method 25 to determine VOC concentration;
(b) EPA Method 1 or 1A for sample and velocity traverses;
(c) EPA Method 2, 2A, 2C, or 2D for velocity and volumetric flow rates;
(d) EPA Method 3 for gas analysis;
(e) EPA Method 4 for stack gas moisture.

Three runs of EPA Method 25 should be made for each stream. The EPA Method 25 results for both streams may be adjusted by the result generated by running a blank (zero air or nitrogen) stream through the sampling train. (No individual result may be adjusted below zero.) The average of the results for each stream should be used in the equation below.

The EPA Method 2, 2A, 2C, or 2D should be run at least twice for each stream. The average of the results for each stream should be used in the equation below. The EPA Methods 3 and 4 should be performed, as applicable, for each run of EPA Method 2, 2A, 2C, or 2D.

The efficiency of the incinerator controlling emissions from bake oven M is equal to:

$$CDE(M) = 1 - \frac{\text{AVG CONC OF OUTLET} * \text{AVG AIRFLOW OUTLET}}{\text{AVG CONC OF INLET} * \text{AVG AIRFLOW INLET}}$$

23 - DELETED

24 - ACCOUNTING FOR CAPTURED PURGED COATING

At the option of the owner/operator, the coating collected by a purge capture system may be subtracted from the amount of each coating used each day. To do this, records must be kept of the number of purge cycles for each coating each day and the standard amount of each coating captured in a purge cycle. The standard amount of coating captured may be established by direct measurement or by calculation of the volume of as sprayed coating in the line(s) being purged.

The total volume of a coating that is captured by the purge capture system on a particular day is:

TCP(I,N) = CP(I) * NPURGE(I,N)

25- RECORDS OF WITHDRAWALS OF COATING FROM MIX TANKS OR CIRCULATING SYSTEMS

If the owner/operator elects to deduct from topcoat usage any quantity of coating that is not consumed in the topcoat operation, then the following documentation is required.

Records must be kept of each withdrawal of coating from mix tanks or circulating system. Withdrawals include discrete removal of coating from the mix tanks or circulating system in ways other than spraying or purging, and coating continuously supplied through the circulating system to operations other than topcoat. Examples of the first type of withdrawal are coating removed for use in final off-line repair or because of quality considerations. An example of the second type of withdrawal is coating supplied through the circulating system to a fascia coating or wheel coating operation.

The records for each coating must include the date of each discrete withdrawal and the volume of coating withdrawn. A sample record is provided in Figure 11. Continuous withdrawals must be accounted for either by establishing standard values for the volume of coating sprayed per part outside of topcoat (e.g. fascia or wheel) or by extending the daily and monthly vehicle coating summaries to include the coating done outside of the topcoat operation.

If the owner/operator chooses not to document withdrawals of topcoat materials not consumed in the topcoat operation, then the quantity of such withdrawals may not be excluded from the calculation of daily topcoat emission rate.

26 - NOTES ON ALTERNATE WEIGHTING FACTORS

The weighting factors presented earlier in this procedure are based on the square footage coated on each vehicle with each coating in each booth. These factors should give an accurate weighting of individual transfer efficiency and bake oven control device VOC loading values in most cases.

If a source owner or operator desires, weighting factors based on the square feet - mils (i.e. surface area coated times dry film build) coated on each vehicle with each coating in each booth may be used. Such weighting factors could be slightly more accurate than weighting factors based solely on square footage.

In cases where there is a separate "interior" color booth in which coating is applied to edges and interior surfaces at a significantly lower dry film build than coating is applied to exterior surfaces in the main color booth, it may be to the sources' advantage to use weighting factors based on square feet - mils. In cases where "interior" coating is done in the main color booth, it is probably to the owner or operator's advantage to use weighting factors based only on square feet coated.

Weighting factors based on square feet - mils should not be used in Sections 27 and 29. Weighting factors based on square footage coated should be used in Sections 27 and 29.

27 - NOTES ON USING COMBINED

BASECOAT/CLEARCOAT TRANSFER EFFICIENCY TEST RESULTS

As noted in the Transfer Efficiency Test Procedure (Sections 18 and 19), some transfer efficiency tests may result in a measured transfer efficiency value for BC/CC combined, rather than individual values for BC and CC. In this case the measured values may be directly used for each BC. That is, for each BC, BTE(I,M) should be set equal to the measured transfer efficiency value for BC(I)/CC. For CC, BTE(CC, M) must be calculated each day from the daily weighted average of the measured transfer efficiency values for each BC/CC combination weighted by the fraction of the total square footage coated in booth M on day N with each BC. These weighting factors are the coating column fractions in the daily vehicle coating summary. On day N:

$$BTE(CC, M) = \frac{\underset{\text{ALL BC}}{\text{SUM}} \; CFRAC(I,M,N)}{\underset{\text{ALL BC}}{\text{SUM}} \; [CFRAC(I,M,N)/BTE(I,M)]}$$

A sample calculation is presented in Figure 21.

28 - NOTES ON USING TRANSFER EFFICIENCY TEST RESULTS WHEN THE TEST ENVELOPE IS MORE THAN ONE BOOTH LONG

Some transfer efficiency tests may span more than one spray booth. For example, an interior color booth and main color booth may be covered by a single test. If a transfer efficiency test spans booths M and M', then BTE(I,M) and BTE(I,M') must be set equal to the test result for coating I.

29 - NOTES ON USING COMBINED BASECOAT/CLEARCOAT BAKE OVEN

CONTROL DEVICE VOC LOADING DATA

As noted in the Test Procedure for Determining Bake Oven Exhaust Control Device VOC Loading for Specific Coatings, at the owner/operator option, control device VOC loading values may be determined for BC/CC combined, rather than individual values for BC and CC. In this case, for each basecoat, set CDL(I,M) equal to the measured value for that basecoat/clearcoat. For clearcoat, CDL(CC,M) must be calculated each day. CDL(CC,M) should be set equal to the daily weighted average of the measured control device VOC loading values for each basecoat/clearcoat weighted by the fraction of the total square footage coated in booth M on day N with each basecoat. These are the coating column fractions in the daily vehicle coating summary.

$$CDL(CC,M) = \frac{\underset{ALL\ BC}{SUM}\ [CDL(I,M) * CFRAC(I,M,N)]}{\underset{ALL\ BC}{SUM}\ [CFRAC(I,M,N)]}$$

A sample calculation is presented in Figure 8.

As noted in the section on Daily Individual Bake Oven Control Device VOC Loading Values (Section 14), as an alternative, TCDL(M,N) can be set equal to the minimum value measured by the test procedure. In this case there would be no need to calculate a separate value, CDL(CC,M), for clearcoat.

30 - NOTES ON ACCOUNTING FOR DILUTION SOLVENT ADDED BY THE COATING MANUFACTURER AT A SATELLITE PAINT PLANT

Some assembly plants have nearby satellite paint plants at which the coating manufacturer may add dilution solvent or other ingredients to coatings before delivering them to the assembly plant. Satellite paint plants frequently deliver coatings to the assembly plant in ready-to-spray condition (i.e. no solvent additions are made at the assembly plant) on a just-in-time basis.

The satellite paint plant must maintain records of all dilution solvent additions and all other additions made before shipping coatings to the assembly plant. The satellite paint plant must also adjust the analytical VOC content, formulation solvent content and volume solids content of each container (drum, tote, etc.) of coating shipped to the assembly plant to account for these additions. These adjustments should be made using calculations similar to those presented in Sections 10, 11 and 12.

31 - CALCULATING FORMULATION WEIGHT FRACTION SOLVENT AS OF SUPPLIED COATING

This section describes the calculations which should be performed to determine the formulation weight fraction solvent content of an as supplied coating. These calculations should be based on the coating manufacturer's formula and batch production records at a point in the coating manufacturing process at and beyond which coating ingredients are mixed or blended only. (No more chemical reactions should take place in the coating manufacturing process.) All materials added before packaging for shipment (e.g., for tinting and adjusting to receive quality control approval) should be included in these calculations.

1 - Set B equal to the number of ingredients in the formula for coating I, including those ingredients added to tint or adjust the coating.

2 - Set WT(I,J,A) equal to the pounds of ingredient A added to the batch of coating I used in addition J. [For ingredients added by volume, WT(I,J,A) can be calculated by multiplying the volume (gallons) added by the density (pounds per gallon) of the ingredient as in Steps 2 through 4 of Section 33. Density should be determined using ASTM D-1475. For dry materials, actual density, not bulk density, should be determined analytically. The density analysis may be performed by the supplier of the ingredient.]

3 - For each ingredient in the formula, determine the weight fraction volatiles, WTVOL (I,J,A), using the appropriate portion of ASTM D-2832. (Note that weight fraction volatiles equals 1 minus weight fraction nonvolatiles.) This information may be provided to the coating manufacturer by the supplier of the ingredient.

32 - CALCULATING FORMULATION SOLVENT CONTENT OF AS SUPPLIED COATING

This section describes the calculations which should be performed to determine the formulation solvent content, CF(I,J), of an as supplied coating.

1 - Determine the density of the coating, DENS(I,J), using ASTM D-1475. (Note, this is the same density analysis made in determining the analytical VOC content of the coating.)

2 - Calculate the formulation solvent content, CF(I,J), of the as supplied coating using the following equation:

$$CF(I,J) = WTFRSV(I,J) * DENS(I,J)$$

33 - FORMULATION VOLUME SOLIDS CONTENT OF AS SUPPLIED COATING

This section describes the calculations which should be performed to determine the formulation volume solids content of an as supplied coating. These calculations should be based on the coating manufacturer's formula and batch production records at a point in the coating manufacturing process at and beyond which coating ingredients are mixed or blended only. (No more chemical reactions should take place in the coating manufacturing process.) All materials added before packaging for shipment (e.g., for tinting or adjusting to receive quality control approval) should be included in these calculations.

1 - Set B equal to the number of ingredients in the formula for coating I, including those ingredients added to tint or adjust the coating.

2 - For ingredients added by weight, set WT(I,J,A) equal to the pounds of ingredient A added to the batch of coating I used in addition J. For ingredients added by volume, set VOL(I,J,A) equal to the gallons of ingredient A added to the batch of coating I used in addition J.

3 - Determine the density, DEN(I,J,A), of each ingredient A in the batch of coating I used in addition J using ASTM D-1475. For dry materials, actual density, not bulk density, should be determined analytically. The units for DEN(I,J,A) are pounds per gallon. This information may be provided to the coating manufacturer by the supplier of the ingredient.

4 - For ingredients added by weight, calculate the volume (gallons) of ingredient A added to the batch of coating I used in addition J using the following equation:

$$VOL(I,J,A) = WT(I,J,A) / DEN(I,J,A)$$

For ingredients added by volume, calculate the weight (pounds) of ingredient A added to the batch of coating I used in addition J using the following equation:

$$WT(I,J,A) = DEN(I,J,A) * VOL(I,J,A)$$

5 - For each ingredient in the formula, determine the weight fraction volatiles, WTVOL(I,J,A), using the appropriate portion of ASTM D-2832. (Note that weight fraction volatiles equals 1 minus fraction nonvolatiles.) This information may be provided to the coating manufacturer by the supplier of the ingredient.

6 - For each ingredient in the formula, determine the density of the volatiles in that ingredient, DVOL(I,J,A). The units for DVOL(I,J,A) are pounds per gallon. This information may be provided to the coating manufacturer by the supplier of the ingredient.

7 - For each ingredient in the formula, determine the volume fraction solids, VFS (I,J,A) using the following equation:

$$VFS(I,J,A) = 1 - \frac{WTVOL(I,J,A) * WT(I,J,A)}{DVOL(I,J,A) * VOL(I,J,A)}$$

8 - As an alternative to steps 5 through 7, the volume fraction solids of an ingredient may be determined directly. This would be particularly useful for ingredients which contain no solids (e.g., solvents) or no volatiles (e.g., dry solids). Ingredients which are thought to be pure liquid resins should be checked as in step 5 to ensure that there are no volatiles (e.g., low molecular weight oligimers) present before concluding that they contain only solids. This information may be provided to the coating manufacturer by the supplier of the ingredient.

9 - Calculate the formulation volume solids content of the as supplied coating using the following equation:

$$VS(I,J) = \frac{\sum_{A=1}^{B} VFS(I,J,A) * VOL(I,J,A)}{\sum_{A=1}^{B} VOL(I,J,A)}$$

34 - RECORDKEEPING REQUIREMENTS

The source owner or operator must maintain at the source, for the time period required by the applicable regulation, all records and calculations used to determine daily VOC emissions from each topcoat operation.

35 - NOTES ON USING THIS PROTOCOL TO DETERMINE THE DAILY VOC EMISSION RATE OF AUTOMOBILE AND LIGHT-DUTY TRUCK SURFACER OPERATIONS

This section reserved for instructions on how to use this protocol to determine the daily VOC emission rate of automobile and light-duty truck surfacer operations.

APPENDIX A

EXAMPLE CALCULATIONS

Figure 1

Spray Booth and Bake Oven Layout for Example Calculations

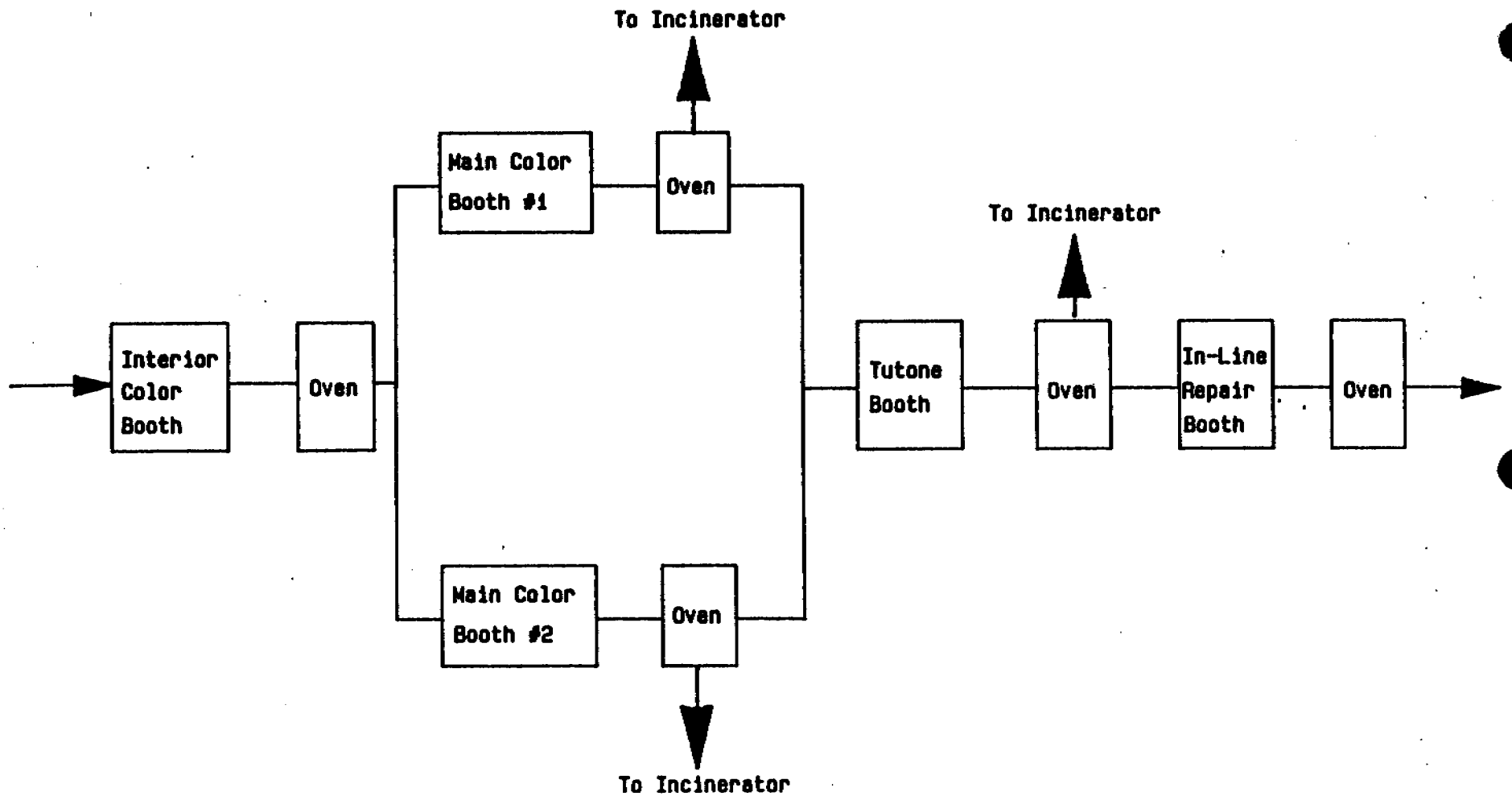


FIGURE 2

Notes on sample coating line and sample calculations

Coatings Used

Red	(R) straight shade
White	(W) base coat
Blue Metallic	(B) base coat
Clear Coat	(CC)

Body Styles

2-door
4-door

Tutones

About half of the red vehicles receive B/CC accent color in tutone booth.

Daily Production

About 800 vehicles per day

The daily calculations are presented for July 14, 19XX. The index (14) indicates the 14th day of the month.

FIGURE 3

(See Section 16)

Individual Vehicle Coating Records - July 14, 19XX

Vehicle ID/Style	Interior		Main Color #1			Main Color #2			Tutone			In-Line Repair		
	Color	Sq Ft	Color	Sq Ft	CC Sq Ft	Color	Sq Ft	CC Sq Ft	Color	Sq Ft	CC Sq Ft	Color	Sq Ft	CC Sq Ft
07140001-2	R	42.0	R	150.0	150.0				B	70.0	70.0			
07140002-2	W	42.0				W	150.0	150.0						
07140003-2	B	42.0	B	150.0	150.0							B	25.0	25.0
07140004-4	B	44.0				B	160.0	160.0						
07140780-4	R	44.0				R	160.0	160.0	B	70.0	70.0			

FIGURE 4

(See Section 16)

Daily Vehicle Coating Summary - July 14, 19XX

Coating	Interior	Main #1	Main #2	Tutone	Repair	Total
R	17200(.213) (.513)	46500(.575) (.625)	15500(.192) (.147)	0(.000) (.000)	1600(.020) (.317)	80800(1.000) (.328)
W	10320(.213) (.308)	6200(.128) (.083)	31000(.639) (.294)	0(.000) (.000)	960(.020) (.190)	48480(1.000) (.197)
B	6020(.142) (.179)	7750(.182) (.104)	13950(.328) (.132)	14000(.330) (.500)	760(.018) (.151)	42480(1.000) (.172)
CC	0(.000) (.000)	13950(.187) (.188)	44950(.602) (.426)	14000(.188) (.500)	1720(.023) (.341)	74620(1.000) (.303)
Total	33540(.136) (1.000)	74400(.302) (1.000)	105400(.428) (1.000)	28000(.114) (1.000)	5040(.020) (1.000)	246380(1.000) (1.000)

Square Feet Coated (Row Fraction)
(Column Fraction)

FIGURE 5

(See Section 15)

Monthly Vehicle Coating Summary - July 19XX

Coating	Square Feet Coated
R	1,535,200
W	1,018,080
B	849,600
CC	1,641,640

FIGURE 6

(See Section 18)

Transfer Efficiency Test Results

Coating	Main Color TE
R	.68
W	.57
B	.47
CC	.74

Each coating was tested because each coating is processed differently. CC was tested separately. See Figure 21 for example with CC tested together with BC.

FIGURE 7

(See Section 20)

Untested Transfer Efficiencies

Coating	Interior	Tutone	Repair
R	.40	NA	.40
W	.40	NA	.40
B	.40	.40	.40
CC	NA	.55	.55

All interior coating is done with air spray. Straight shades and basecoats are applied by air spray in tutone and repair booths. Clearcoat is applied by electrostatic spray in tutone and repair booths.

FIGURE 8

(See Section 21)

Bake Oven Exhaust Control Device VOC Loading - Panel Test Results

Coating	Main Color	Tutone
R	2.0	NA
W/CC	2.3	NA
B/CC	2.1	2.0

Calculation of separate value for main color CC for July 14, 19XX. (See section 29.)

Main #1

$$\frac{(2.3)(.083) + (2.1)(.104)}{.083 + .104} = 2.2$$

Main #2

$$\frac{(2.3)(.294) + (2.1)(.132)}{.294 + .132} = 2.2$$

FIGURE 9

(See Section 22)

Bake Oven Exhaust Incinerator Efficiency Test Results

Main #1	96%
Main #2	96%
Tutone	94%

FIGURE 10

(See Section 13)

Daily Weighted TE for July 14, 19XX

$$R \quad \frac{1}{\frac{.213}{.40} + \frac{.575}{.68} + \frac{.192}{.68} + \frac{.020}{.40}} = \frac{1}{1.710} = .585$$

$$W \quad \frac{1}{\frac{.213}{.40} + \frac{.128}{.57} + \frac{.639}{.57} + \frac{.020}{.40}} = \frac{1}{1.928} = .519$$

$$B \quad \frac{1}{\frac{.142}{.40} + \frac{.182}{.47} + \frac{.328}{.47} + \frac{.330}{.40} + \frac{.018}{.40}} = \frac{1}{2.31} = .433$$

$$CC \quad \frac{1}{\frac{.187}{.74} + \frac{.602}{.74} + \frac{.188}{.55} + \frac{.023}{.55}} = \frac{1}{1.45} = .690$$

FIGURE 11

(See Section 10, 11, 12 and 25)

Monthly Additions for Red - July 19XX

Start 1510
End 1210

		Coating				Diluent	
Date	Batch	Gal PADD	Formula CF	Analytical CA	Formula Vol Solids VS	Gal RADD	Density RD
7/1	A	1000	3.70	4.00	.47	50	6.8
7/3	A	600	3.70	4.00	.47		
7/7	A	850	3.70	4.00	.47	60	6.8
7/9	B	1000	3.60	3.90	.48		
7/12	B	850	3.60	3.90	.48	60	6.8
7/15	C	800	3.80	4.20	.46		
7/18	C	700	3.80	4.20	.46	60	6.8
7/21	C	1000	3.80	4.20	.46		
7/24	D	900	3.60	3.90	.48	50	6.8
7/28	D	1000	3.60	3.90	.48		
7/30	D	1000	3.60	3.90	.48	60	6.8
		9700				340	

Withdrawals for Red - July 19XX.

Date	Gal	Destination
7/12	50	Final repair

FIGURE 12

(See Section 17)

Monthly Coating Usage - July 19XX

Coating	Gallons	Formula (RCF)	Analytical* (RCA)	Vol Solids (RVS)
R	10290	3.78	4.10	.456
W	3500	4.11	4.32	.423
B	3400	4.49	4.72	.359
CC	4200	3.31	3.65	.527

For red, monthly usage = 1510 - 1210 + 9700 + 340 - 50 = 10290
The data for this calculation came from Figure 11.

* See Figure 13 for sample calculation.

FIGURE 13

(See Section 10)

Analytical VOC Content of as Applied Red Coating - July 19XX

Coating Additions

Gallons PADD(I,J)	x	Test VOC CA(I,J)	=	Total VOC
1000		4.00		4000
600		4.00		2400
850		4.00		3400
1000		3.90		3900
850		3.90		3315
800		4.20		3360
700		4.20		2940
1000		4.20		4200
900		3.90		3510
1000		3.90		3900
1000		3.90		3900
9700				38825

Diluent Additions

Gallons PADD(I,K)	x	Density RD(I,K)	=	Total VOC
50		6.8		340
60		6.8		408
60		6.8		408
60		6.8		408
50		6.8		340
60		6.8		480
340				2312

$$RCA(I) = \frac{38825 + 2312}{9700 + 340} = 4.10$$

FIGURE 14

(See Section 8)

Daily Coating Usage - July 14, 19XX

Coating I	Month's Usage GMON(I)	x	Day's Sq. Ft. DAYSQFT(I,14)	/	Month's Sq. Ft. MONSQFT(I)	=	Day's Usage GDAY(I,14)
R	10290		80800		1535200		541.6
W	3500		48480		1018080		166.7
B	3400		42480		849600		170.0
CC	4200		74620		1641640		190.9

FIGURE 15

(See Section 9)

VOC Generated per Gallon of as Applied Coating Used - July 14, 19XX

Coating I	Formula RCF(I)	x	1-TE	+	Analytical RCA(I)	x	TE TE(I,14)	=	VOC Gen RCV(I,14)
R	3.78		.415		4.10		.585		3.97
W	4.11		.481		4.32		.519		4.22
B	4.49		.567		4.72		.433		4.59
CC	3.31		.310		3.65		.690		3.55

FIGURE 16

(See Section 5)

Total Daily VOC Generated - July 14, 19XX

Coating I	Gallons GDAY(I,M)	x	VOC/Gal RCV(I,14)	=	VOC Generated (Pounds)
R	541.6		3.97		2150.2
W	166.7		4.22		703.5
B	170.7		4.59		780.3
CC	190.9		3.55		677.7
Total					4311.7 = DVG(14)

FIGURE 17

(See Section 6)

Total Daily Volume Solids Deposited - July 14, 19XX

Coating I	Gallons GDAY(I,M)	x	Vol Solids RVS(I)	x	Daily TE TE(I,14)	=	Solids Dep (Gallons)
R	541.6		.456		.585		144.5
W	166.7		.423		.519		36.6
B	170.0		.359		.433		26.4
CC	190.9		.527		.690		69.4
Total							276.9 = DSD(14)

FIGURE 18

(See Section 14)

Daily Individual Bake Oven Exhaust Control Device VOC Loading Values

Main #1 $2.0(.625) + 2.3(.083) + 2.1(.104) + 2.2(.188) = 2.07$

Main #2 $2.0(.147) + 2.3(.294) + 2.1(.132) + 2.2(.426) = 2.19$

Tutone $= 2.00$

FIGURE 19

(See Section 7)

Total Daily Bake Oven Exhaust Control Credit - July 14, 1988

Booth/Oven	VOC Loading TCDL(M,14)	Control Eff CDE(M)	Wtg Factor BRFRAC(M,14)	Control Credit
Main #1	2.07	.96	.302	.60
Main #2	2.19	.96	.428	.90
Tutone	2.00	.94	.114	.21
Total				1.71 = DCC(14)

FIGURE 20

(See Section 4)

Daily VOC Emission Rate Calculation - July 14, 19XX

$$DER(14) = [DVG(14)/DSD(14)] - DCC(14)$$

$$= [4311.7/276.9] - 1.71$$

= 13.86 pounds VOC per gallon solids deposited

FIGURE 21

(See Section 27)

Calculating CC TE from combined BC/CC Transfer Efficiency Test Results

TE test results

W/CC .640

B/CC .580

CC TE for July 14, 19XX

Main Color Booth #1

$$BTE(CC, Main\ 1) = \frac{.083 + .104}{\frac{.083}{.640} + \frac{.104}{.580}} = \frac{.187}{.309} = .605$$

Main Color Booth #2

$$BTE(CC, Main\ 2) = \frac{.294 + .132}{\frac{.294}{.640} + \frac{.132}{.580}} = \frac{.426}{.687} = .620$$

FIGURE 22

(See Section 16)

Sample Calculation of Equivalent Vehicles

Vehicle	Process Step	Square Feet Coated	Equivalent Vehicles
2-Door Sedan	Main Color	184	0.92
	Tutone	10	0.05
4-Door Sedan	Main Color	200	1.00
	Tutone	12	0.06
Station Wagon	Main Color	229	1.15
	Tutone	17	0.09

In this sample, the "base vehicle" is the 4-Door Sedan Main Color step. (200 square feet coated is equated to 1.00 equivalent vehicle.)

FIGURE 23

(See Section 16)

Sample Calculation of 4 Percent Standard Daily Repair Rate

Using data for red (R) coating in Figure 4:

Booth	Square Feet Coated
Interior	17200
Main #1	46500
Main #2	15500
Total (excluding repair)	79200

Repair Square Feet Coated = 79200 * 0.04 = 3168

Total (including repair) = 79200 + 3168 = 82368

FIGURE 24

(See Section 19)

Pilot Line TE Test Data Validation

	In-Plant	Pilot
Wt solids sprayed/vehicle	2.80 lbs	3.10 lbs
Average Class I film build	2.20 mils	2.00 mils
Average Class II film build	1.30 mils	1.50 mils
Overall average film build	1.90 mils	1.83 mils

Solids sprayed test $\frac{3.10 - 2.80}{3.10} * 100 = +9.7\%$ OK

Overall film build change $\frac{1.83 - 1.90}{1.90} * 100 = -3.7\%$ OK

Consistency of solids sprayed and overall film build $ABS[9.7 - (-3.7)] = 13.4 \leq 20$ OK

FIGURE 25

(See Section 19)

Calculation of Pilot Line TE

Weight solids sprayed per vehicle (pilot) 3.10 lbs

Weight solids deposited per vehicle (pilot) 1.98 lbs

$$\text{Pilot TE} = \frac{1.98}{3.10} = 0.64$$

FIGURE 26

(See Section 19)

Calculation of Adjusted Pilot Line TE

Weight solids sprayed per vehicle (pilot) 3.10 lbs

Weight solids sprayed per vehicle (plant) 2.80 lbs

Overall average dry film build (pilot) 1.83 mils

Overall average dry film build (plant) 1.90 mils

Pilot TE = 0.64

$$\text{Adjusted Pilot TE} = 0.64 * \frac{3.10}{2.80} * \frac{1.90}{1.83} = 0.74$$

ADDED 11/88

FIGURE 27

(See Section 19)

Annual Revalidation and Readjustment of Pilot Line TE Test Data

	New In-Plant	Old Pilot
Wt solids sprayed/vehicle	3.20 lbs	3.10 lbs
Average Class I film build	2.0 mils	2.0 mils
Average Class II film build	1.3 mils	1.5 mils
Overall average film build	1.77 mils	1.83 mils

Solids sprayed test $\frac{3.10 - 3.20}{3.20} * 100 = -3.1\%$ OK

Overall film build change $\frac{1.83 - 1.77}{1.77} * 100 = +3.4\%$ OK

Consistency of solids sprayed and overall film build ABS(-3.1 - 3.4) = 6.7 $\leq$ 20 OK

New Adjusted Pilot TE = $0.64 * \frac{3.10}{3.20} * \frac{1.77}{1.83}$

= 0.60

ADDED 11/88

FIGURE 28

(See Section 19)

Determination of Required Number of Dry Film Build Measurements for Vehicle with Plastic Parts

	Square Footage Coated		
	"Magnetic" (Steel)	"Non-Magnetic" (Plastic)	Total
Class I	110	40	150
Class II	70	10	80
Total	180	50	230

Percent non-magnetic area $\frac{50}{230} * 100 = 22\% < 25\%$

Therefore, dry film build measurements are not needed on non-magnetic areas.

The required number of before and after measurements per vehicle are:

150 on 110 square feet of magnetic Class I area

160 on 70 square feet of magnetic Class II area (160 = 80 * 2)

FIGURE 28 (Continued)

Square Footage Coated

	"Magnetic" (Steel)	"Non-Magnetic" (Plastic)	Total
Class I	90	60	150
Class II	70	10	80
Total	160	70	230

Percent non-magnetic area $\frac{70}{230} * 100 = 30\% > 25\%$

Therefore, dry film build measurements are required on non-magnetic areas.

The required number of before and after measurements per vehicle are:

150 on 150 square feet of Class I area

160 on 80 square feet of Class II area

FIGURE 29

(See Section 19)

Calculation of Overall Average Dry Film Build

	Square Feet Coated
Class I	150
Class II	80
Total	230

Overall average dry film build equals:

$$\frac{\text{average Class I dry film build} * 150}{230} + \frac{\text{average Class II dry film build} * 80}{230}$$

APPENDIX B

SUMMARY OF ADDITIONS AND REVISIONS TO JUNE 10, 1988 VERSION OF PROTOCOL

Revised Section 18 added November 1988.

Scope moved from page 18-2 to 18-1.

New language in paragraph B on page 18-2.

No changes on page 18-3.

New item 6 at top of page 18-4.

One line moved from page 18-4 to 18-5, and one sentence moved from page 18-6 to 18-5.

New language in Frequency of Certification on page 18-6.

New Section 19 added November 1988.

Adds pilot line transfer efficiency test procedure to protocol.

Revised page 33-3 added November 1988.

Adds denominator to equation in Part 9.

New Figures 24 - 29 added November 1988.

These figures illustrate new Section 19 also added November 1988.

New page iii added December 1988.

Adds Appendix A (Example Calculations)
and Appendix B (Summary of Additions and Changes) to table of contents. The example calculations were previously in a separately bound volume.

Revised page 1-2 added December 1988.

New language in first sentence to indicate that example calculations are in Appendix A.

Adds paragraph about agency review of owner/operator selected conditions and parameters.

Adds paragraph which notes that changes and additions from original June 10, 1988, version are summarized in Appendix B.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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EPA-450/3-88-018		

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	6. PERFORMING ORGANIZATION CODE
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U.S. Environmental Protection Agency Emission Standards Division Office of Air Quality Planning and Standards Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This protocol determines the daily VOC emission rate (pounds of VOC per gallon of coating solids deposited) for a complete automobile and light-duty truck topcoat operation. The protocol is designed for use in cases where (1) the topcoat emission limit is stated in units of pounds of VOC per gallon of solids deposited, (2) compliance is to be demonstrated for each day, and (3) the entire topcoat operation (i.e., all spray booths, flash-off areas and bake ovens where topcoat is applied, dried, and cured; except final off-line repair) is treated as a single entity.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Automobile Topcoat Light-Duty Truck Topcoat Volatile Organic Compound Emissions		

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December 1978

Air

EPA

Control of Volatile Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements in Agency documents in metric units. Dual units are sometimes given in the text for clarity. Listed below are abbreviations and conversion factors for English equivalents of metric units. Frequently used measurements are also presented in dual units below for the reader's convenience.

METRIC UNIT	ALTERNATE UNIT	CONVERSION
centimeter (cm)	inches	cm x 0.394 = in
Pascals (Pa)	atmospheres	Pa x 9.87×10^{-6} = atm
	inches of water	Pa x 4.02×10^{-3} = inches of water
liters (l)	gallons	l x 0.264 = gal

FREQUENTLY USED MEASUREMENTS

750 pascals ∿ 3 inches of water

1500 pascals ∿ 6 inches of water

4500 pascals ∿ 18 inches of water

6250 pascals ∿ 25 inches of water

2.5 cm ∿ 1 inch

.625 cm ∿ 1/4 inch

20,000 liters ∿ 5280 gallons

I. BACKGROUND

This guideline is related to the control of volatile organic compounds (VOC) from gasoline tank trucks and vapor collection systems at bulk terminals, bulk plants and service stations. Guideline documents have already been published on bulk plants,[1] bulk terminals[2] and service stations.[3] The intent of this guideline is to define leak tight conditions and related test procedures for vapor collection systems and tank trucks while loading and unloading at these facilities. VOC emitted from leaks in collection equipment are primarily C_4 and C_5 paraffins and olefins which are photochemically reactive (precursors to oxidants).

Methodology described in this guideline represents the presumptive norm or reasonably available control technology (RACT) that can be applied to an existing facility. RACT is defined as the lowest emission limit that a particular source is capable of meeting by the application of control technology that is reasonably available considering technological and economic feasibility. It may require technology that has been applied to similar, but not necessarily identical, source categories. It is not intended that extensive research and development be conducted before a given control technology can be applied to the source. This does not, however, preclude requiring a short-term evaluation program to permit the application of a given technology to a particular source. This latter effort is an appropriate technology-forcing aspect of RACT.

A. NEED TO REGULATE

Control techniques guidelines are being prepared for source categories that emit significant quantities of air pollutants in areas of the country

where National Ambient Air Quality Standards (NAAQS) are not being attained. Vapor balance and processor systems have been applied to bulk plants, terminals, and service stations in many areas of the nation. Leaks from tank trucks and vapor collection systems should be minimized to ensure that vapor control systems at these systems function effectively.

B. CONTROL APPROACH

The approach described in this document is to ensure that good maintenance practices are followed. Maintenance would be enforced through the surveillance and periodic testing of suspect leak points. It should be noted that while some leak sources (such as vapor piping joints) may stay in leak tight condition for extended periods of time, others (such as pressure and vacuum vents, and hatch seals) may leak shortly after maintenance. It is expected that compliance with the suggested control measure will in some cases require replacement of truck pressure and vacuum vents and dome covers. In addition, a greater degree of surveillance and maintenance will be needed at bulk plants and terminals equipped with top loading (vapor head) systems than at those using bottom loading. Additional information on control techniques, costs, and monitoring procedures is presented in an EPA report.[4]

II. REGULATORY APPROACH

A. AFFECTED FACILITIES

The two separate affected facilities are gasoline tank trucks that are equipped for vapor collection and the vapor collection systems at bulk terminals, bulk plants, and service stations that are equipped with vapor balance and/or vapor processing systems.

B. RECOMMENDED REGULATION

B.1 Gasoline Tank Trucks

Gasoline truck tanks and their vapor collection systems shall not sustain a pressure change of more than 750 pascals (3 inches of H_2O) in 5 minutes when pressurized to 4500 pascals (18 inches of water) or evacuated to 1500 pascals (6 inches of water) using the test procedure described in Appendix A. In addition, there are to be no avoidable visible liquid leaks. Invariably there will be a few drops of liquid from disconnection of dry breaks in liquid lines even when well maintained; these few drops should be allowed.

B.2 Vapor Collection Systems

B.2.1 - During loading or unloading operations at service stations, bulk plants and bulk terminals, there shall be no reading greater than or equal to 100 percent of the lower explosive limit (LEL, measured as propane) at 2.5 centimeters around the perimeter of a potential leak source as detected by a combustible gas detector using the test procedure described in Appendix B. In addition, there are to be no avoidable visible liquid leaks. Invariably there will be a few liquid drops from the disconnection of well maintained bottom loading dry breaks and the raising of well maintained top loading vapor heads; these few drops should be allowed. The vapor collection system includes all piping, seals, hoses, connections, pressure-vacuum vents, and other possible leak sources between the truck and the vapor processing unit and/or the storage tanks and vapor holder; and

B.2.2 - The vapor collection and vapor processing equipment must be designed and operated to prevent gauge pressure in the tank truck from exceeding 4500 pascals (18 inches of water) and prevent vacuum from exceeding 1500 pascals (6 inches of water).

C. MONITORING REQUIREMENTS

C.1 Gasoline Tank Trucks

Gasoline truck tanks must be certified leak tight as described in Section B.1 annually.

In addition, truck tanks can be monitored by regulatory agencies as needed during loading and unloading using the combustible gas detection procedure described in B.2.1, provided that the requirements in Section B.2.2 are met. Trucks with leaks greater than or equal to 100 percent of the LEL are to be repaired within 15 days and be required to take and pass the pressure and vacuum test described in Section B.1 The truck tank and its vapor collection system includes all piping, seals, hoses, connections, hatch covers, pressure vacuum vents, vapor hoods and other possible leak sources on the truck tank.

C.2 Vapor Collection Systems

Vapor collection systems can be monitored by regulatory agencies as needed using the combustible gas detection procedure described in B.2.1.

D. RECORD KEEPING AND REPORTING REQUIREMENTS

D.1 Gasoline Tank Trucks

Each truck must have a sticker displayed on each tank indicating the identification number of the tank and the date each tank last passed the pressure and vacuum test described in Section B.1. This sticker must be located near the Department of Transportation Certification plate (DOT, Title 49, Part 178.340-10b).

D.2 Vapor Collection System

Bulk terminal, bulk plant and service station owners or operators must keep records for two years indicating the last time the vapor collection facility

passed the requirements described in B.2 and identifying points at which VOC leakage exceeded the provisions of Section B.2.1.

E. OTHER CONSIDERATIONS

Presently, there is limited information available on the amount of monitoring necessary to ensure that leaks are kept to the limits described above. Therefore, regulations should allow for modifications in the monitoring schedule when experience proves it to be either inadequate or excessive. If, after over one year of monitoring, i.e., at least two complete annual checks, the operator of an affected facility feels that modifications of the requirements are in order, he may request in writing to the air pollution control officer that a revision be made. The submittal should include data that have been developed to justify any modifications in the monitoring schedule. On the other hand, if the air pollution control officer finds an excessive number of leaks during an inspection, or if the operator finds an excessive number of leaks during scheduled monitoring, consideration should be given to increasing the frequency of inspections.

III. COMPLIANCE TEST METHOD AND MONITORING TECHNIQUES

The measurement procedures that were developed for determining leak tightness of truck tanks and vapor control systems at bulk terminals, bulk plants, and service stations, are discussed in this section. The presentation covers the various methods considered with the advantages and disadvantages of each, testing problems encountered, and the accuracy, reliability, and allowable modifications of the recommended methods.

A. COMPLIANCE TEST METHOD DESCRIPTION

A.1 General Description and Background

The recommended compliance test method as detailed in Appendix A can be used to determine the leak-tightness of gasoline truck tanks. Pressure and vacuum are applied to the tanks of a gasoline delivery truck and the change in pressure/vacuum is recorded after a specified period of time. The recommended regulation in Section II.B.1 in effect defines a "leak tight condition" which is equivalent to 99 percent recovery efficiency during vapor transfer from a truck tank. The recommended compliance procedure is actually an equipment performance criteria rather than a true emission measurement test. However, emissions from a truck tank can be estimated from the known required degree of leak-tightness.

Developmental work on a leak test method was performed by the California Air Resources Board (CARB), San Diego Air Pollution Control District (SDAPCD), and Standard Oil of California, among others. Leak-tightness regulations have been in effect in California for over two years. The pressure and vacuum limits recommended in Section II.B.1 are based on a consensus of the above mentioned groups, and on an EPA field testing program which was conducted in order to evaluate the leak test method and performance criteria. The study shows that EPA's recommended performance criteria is realistic and achievable and the test method is inexpensive, reliable, and repeatable.[5]

A.2 Modifications

There are two areas of common modifications to the test procedure in Appendix A.

The recommended EPA compliance test procedure uses air to pressurize and evacuate the truck tank. In EPA field testing, this was

found to be the most convenient and inexpensive procedure. However, some owners prefer loading and draining the tank with a liquid, usually diesel fuel or water, to create the required pressure and vacuum. This is an acceptable and equivalent alternative.

The EPA procedure also requires that gasoline vapors be purged from the truck tank before conducting the leak-tightness test. This is easily accomplished by carrying a diesel load immediately prior to the compliance test or blowing air into the tank with the dome lids open. Gasoline vapors in the tank cause testing inconsistencies. With volatile vapors, the tank pressure varies more readily with slight changes in temperature. However it is possible to test without purging the gasoline vapors if there is enough time for the vapors to stabilize and reach a constant temperature in the covered testing area. One can ensure that the vapors have stabilized and are not affecting the test results by conducting the test two times with the same results.

A.3 Effectiveness

The EPA field testing program[6] and a recent CARB study[7] both indicate that truck tanks rarely remain in a leak-tight condition within two or three months after the compliance test. After the initial leak-tightness compliance test, the leaks that occur are usually easily detectable and correctable with good normal maintenance. It is hoped that conducting unannounced spot-checks with monitoring procedures described in the following section, will encourage more frequent and effective maintenance.

B. DESCRIPTION OF MONITORING TECHNIQUES

B.1 Background

Monitoring techniques for leak detection were developed to ensure the continuing existence of leak-tight conditions between compliance tests. A test method was sought that would give pass/fail compliance information for leakage from truck tanks and vapor control systems at bulk terminals, bulk plants, and service stations. It was desired that the monitoring test method be low cost, quick, and used without disturbing normal operations. It is essential that leak detection by a monitoring technique be be equivalent to the leak-tightness criteria of the pressure/vacuum compliance test.

Several leak detection monitoring methods were investigated in EPA's field testing program: combustible gas detector, sonic detector, bubble indication, sensory detection (i.e., sound, sight, smell, touch), vapor to liquid volume ratio, quick leak decay, and bag capture. Bag capture and combustible gas detector were both found to be reliable, quick, low cost, and closely equivalent to the compliance criteria. The recommended method is the combustible gas detector procedure because it is more reliable and can be applied to top and bottom-loaded tanks. However, the bag capture procedure is an acceptable alternative for leak detection of bottom-loaded tanks. A discussion of the other non-recommended methods is included in an EPA contractor report.[8]

B.2 Description of Combustible Gas Detector Procedure

B.2.1 - Selection and applicability. The combustible gas detector is the recommended leak detection method because it is simple, quick, inexpensive, reliable, and non-subjective. It can be used for leak

detection of truck tanks and vapor control systems without disturbing normal operations. Although a combustible gas detector is often considered a qualitative monitoring instrument, the detailed specifications of its use and operation, as defined in Appendix B, make this an acceptable procedure.

Leak detection of truck tanks by combustible gas detector correlates well with the pressure/vacuum compliance criteria in Section II.B.1, when a leak is defined as a meter reading greater than or equal to 100 percent LEL as propane. The monitoring procedure will correctly identify 42 percent of the non-complying tanks, while incorrectly identifying only 5 percent of the complying tanks.[9] The combustible gas detector procedure is purposely designed to detect gross violations of the leak-tightness performance criteria, but will not confirm compliance, i.e. tanks with marginal violations will evade detection.

B.2.2 - Equipment and operation specifications. In order to make leak detection by combustible gas detector more reliable and repeatable, equipment and operation specifications are tightly defined. For valid monitoring, it is important that the procedure is the same as the one used in EPA's field testing and data collection.

Equipment specifications require that the meter is calibrated to propane, inside probe diameter is 0.625 cm (1/4 inch), and response time for full-scale deflection with the sampling probe and line attached is less

than 8 seconds. A standard calibration gas is needed to standardize the detector response. The selection of propane as the calibration gas is arbitrary. Propane was used for calibration in the data gathering tests, and it is probably the most readily available gas.

The probe diameter requirement allows some dilution air drawn in if the leak is very small, and thus the detector will not register a leak. If the same leak were sampled with a smaller diameter probe, the sample line would be filled with leaked vapors with no dilution, and a leak would be detected. Thus, a larger probe diameter ensures that only insignificant leaks are registered.

The response time requirement ensures that the meter pump is strong enough to draw the sample quickly through the sampling probe and line. This quick response is necessary since there is little time during a loading to check all potential sources of leakage.

Operation of the combustible gas detector for leak monitoring is also tightly defined to eliminate variability. However, any arbitrariness or sloppiness in the procedure is in favor of the truck tank owner. Operation specifications require measurement at 2.5cm (1 inch) distance from the leak source, positioning the probe in the path of (parallel to) the vapor flow, moving the probe slowly locating the point of highest meter response, and blocking wind interference when possible. Measurement at 2.5cm distance allows some dilution if only a very small leak exists. The distance can be maintained during monitoring by putting a 2.5cm extension on the probe tip. Maintaining this distance is essential or else insignificant leaks will be detected.

Higher meter readings will be obtained when the probe is properly positioned, moved slowly, and if care is taken to locate the center of a leak. These specifications were followed diligently in the testing which was used to develop the data base and correlation with the compliance test.

Any sloppiness in these areas would detect less leaks and be in favor of the truck. Furthermore, the field testing was conducted on windless, hot days. Winds would dilute the vapors before detection, and cooler temperatures would reduce the hydrocarbon concentration. Again, under these conditions, the meter would detect less leakage, and the variability in the method favors the truck tank owners.

B.2.3 - Modifications. It should be noted that the adequacy of the combustible gas detector method, and the LEL level where the method is usable, are based on the performance test criteria in Section II.B.1. If other criteria are used to define a leak-tight tank, the detector method will have to be re-evaluated to determine the applicable LEL level to be used for monitoring.

The combustible gas detector method can be made less stringent by simply increasing the sampling distance. However, this is not recommended since the purpose of monitoring is to ensure compliance, and the recommended procedure is closely equivalent to the leak-tightness performance test.

B.3 Description of Bag Capture Procedure

B.3.1 - Background. The bag capture procedure is an acceptable alternative method for leak monitoring of bottom-loaded truck tanks. The complete procedure is included in Appendix C. The procedure was developed by San Diego Air Pollution Control District, and has been in use for over two years. The volume of leakage is measured directly by placing calibrated bags over all dome covers. The volume of allowable leakage is calculated from the parameters of the pressure/vacuum compliance test (as shown in equation 7.1, Appendix C).

This procedure, like the combustible gas detector, is designed to detect gross violations while not detecting marginal violations. Again, any sloppiness or variability in the method is in the favor of the truck tank. Only leakage from dome covers, hatches, and relief valves is captured; leakage from the tank vapor collection system is not included. If the seal between the bag apparatus and tank is not tight enough, the leakage may be underestimated. Furthermore, the allowable volume of leakage is based on 4500 pascals (18 inches H_2O) pressure, which rarely occurs during loadings.

B.3.2 - Disadvantage and Advantages. This method does have serious drawbacks. It can only be applied to bottom-loaded tanks. Some tanks cannot be monitored because the equipment configuration prevents a tight seal. Also, not all potential leakage sources are monitored.

On the other hand, the method has some real advantages. The equipment is very inexpensive and easy to use. It can be applied regardless of the type of vapors inside. Emissions can be measured directly, instead of by estimation. In San Diego, with this method, a leak has never been incorrectly detected for a complying tank. Finally, the bag method can be modified to detect leaks for any degree of leak-tightness if the parameters of the performance test are altered.

Many agencies and companies resist the use of a combustible gas detector. The bag capture method is a good alternative. It is probably less stringent than the explosimeter, but it will still detect all gross violations.

C. VAPOR CONTROL SYSTEM MONITORING

C.1 Pressure and Vacuum Limits.

The regulation in Section II.B.2.2 requires that the pressure/vacuum in a vapor control system remain within the pressure/vacuum limits of the truck tank compliance test. This ensures that a vapor control system will not create a leak on a tank. During leak detection monitoring of the tanks, the pressure must remain within these limits or else the detection of any leak will be invalidated.

C.2 Leak Detection.

The combustible gas detector procedure in Appendix B can be applied to potential sources of leakage at terminal, plant, and service station vapor control systems. These points of leakage can be easily identified and corrected during normal maintenance, and once corrected remain in leak tight condition for extended periods of time.

This application of the combustible gas detector procedure is a qualitative measurement; there is no way to relate this leak detection to emission levels.

IV. REFERENCES

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5. "Leak Testing of Gasoline Tank Trucks," Scott Environmental Technology, Inc., prepared for U.S. EPA, Emission Standards and Engineering Division, Draft report, August 10, 1978.

6. Reference 4, Op. Cit.

7. "Investigation of the Compliance of Vapor Recovery Equipment at Gasoline Bulk Terminals in the South Coast Air Quality Management District and Kern County Air Pollution Control District," State of California Air Resources Board, Report No. LE-78-003, November 8, 1978.

8. Reference 4, Op. Cit.

9. Reference 4, Op. Cit.

APPENDIX A

PRESSURE-VACUUM TEST PROCEDURES
FOR LEAK TIGHTNESS OF TRUCK TANKS

1. PRINCIPLE

Pressure and vacuum are applied to the compartments of gasoline truck tanks and the change in pressure/vacuum is recorded after a specified period of time.

2. APPLICABILITY

This method is applicable to determining the leak tightness of gasoline truck tanks in use and equipped with vapor collection equipment.

3. DEFINITIONS

3.1 Truck tank. Any container, including associated pipes and fittings, that is used for the transport of gasoline.

3.2 Compartment. A liquid-tight division of a truck tank.

3.3 Truck tank vapor collection equipment. Any piping, hoses, and devices on the truck tank used to collect and route the gasoline vapors in the tank to the bulk terminal, bulk plant, or service station vapor control system.

4. APPARATUS

4.1 Pressure source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the truck tank to 6250 pascals (25 inches H_2O) above atmospheric pressure.

4.2 Regulator. Low pressure regulator for controlling pressurization of the truck tank.

4.3 Vacuum source. Vacuum pump capable of evacuating the truck tank to 2500 pascals (10 inches H_2O) below atmospheric pressure.

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4.4 Manometer. Liquid manometer, or equivalent, capable of measuring up to 6250 pascals (25 inches H_2O) gauge pressure with $\pm$ 25 pascals ($\pm$ 0.1 inch H_2O) precision.

4.5 Test cap for vapor recovery hose fittings. This cap should have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure/vacuum supply hose.

4.6 Pressure/vacuum relief valves. The test apparatus shall be equipped with an in-line pressure/vacuum relief valve set to activate at 7000 pascals (28 inches H_2O) above atmospheric pressure or 3000 pascals (12 inches H_2O) below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

4.7 Caps for liquid delivery line.

4.8 Pressure/vacuum supply hose.

5. PRETEST CONDITION

5.1 Purging of vapor. The truck tank shall be purged of gasoline vapors and tested empty. The tank may be purged by any safe method such as flushing with diesel fuel or heating fuel.

5.2 Location. The truck tank shall be tested where it will be protected from direct sunlight.

6. TEST PROCEDURE

6.1 The dome covers are to be opened and closed.

6.2 Connect static electrical ground connections to tank. Attach the delivery and vapor hoses, remove the delivery elbows, and plug the liquid delivery fittings.

6.3 Attach the test cap to the vapor recovery line of the truck tank.

6.4 Connect compartments of the tank internally to each other if possible. (If not possible, each compartment must be tested separately.)

6.5 Connect the pressure/vacuum supply hose and the pressure/vacuum relief valve to the shut-off valve. Attach the pressure source to the hose. Attach a manometer to the pressure tap.

6.6 Open the shut-off valve in the vapor recovery hose cap. Applying air pressure slowly, pressurize the tank, or alternatively the first compartment, to 4500 pascals (18 inches H_2O).

6.7 Close the shut-off valve and allow the pressure in the truck tank to stabilize, adjusting the pressure if necessary to maintain 4500 pascals (18 inches H_2O). When the pressure stabilizes, record the time and initial pressure.

6.8 At the end of 5 minutes, record the time and final pressure.

6.9 Disconnect the pressure source from the pressure/vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

6.10 Connect the vacuum source to the pressure/vacuum supply hose.

6.11 Slowly evacuate the tank, or alternatively the first compartment, to 1500 pascals (6 inches H_2O).

6.12 Close the shut-off valve and allow the pressure in the truck tank to stabilize, adjusting the pressure if necessary to maintain 1500 pascals (6 inches H_2O) vacuum. When the pressure stabilizes, record the time and initial pressure.

6.13 At the end of 5 minutes, record the time and final pressure.

6.14 Repeat steps 6.5 through 6.13 for each compartment if they were not interconnected.

7. ALTERNATIVE TEST METHODS

Techniques, other than specified above, may be used for purging and pressurizing the truck tanks, if prior approval is obtained from the air pollution control officer. Such approval will be based upon demonstrated equivalency with the above method.

APPENDIX B

GASOLINE VAPOR LEAK DETECTION PROCEDURE
BY COMBUSTIBLE GAS DETECTOR

1. PRINCIPLE

A combustible gas detector is used to indicate any incidence of leakage from gasoline truck tanks and vapor control systems. This qualitative monitoring procedure is an enforcement tool to confirm the continuing existence of leak-tight conditions.

2. APPLICABILITY

This method is applicable to determining the leak-tightness of gasoline truck tanks during loading without taking the truck tank out of service. The method is applicable only if the vapor control system does not create back-pressure in excess of the pressure limits of the truck tank compliance leak test. For vapor control systems, this method is applicable to determining leak-tightness at any time.

3. DEFINITIONS

3.1 Truck tank. Any container, including associated pipes and fittings, that is used for the transport of gasoline.

3.2 Truck tank vapor collection equipment. Any piping, hoses, and devices on the truck tank used to collect and route the gasoline vapors in the tank to the bulk terminal, bulk plant, or service station vapor control system.

3.3 Vapor control system. Any piping, hoses, equipment, and devices at the bulk terminal, bulk plant, or service station, which is used to collect, store, and/or process gasoline vapors.

4. APPARATUS AND SPECIFICATIONS

4.1 Manometer. Liquid manometer, or equivalent, capable of measuring up to 6250 pascals (25 inches H_2O) gauge pressure with $\pm$25 pascals (0.1 inch H_2O) precision.

4.2 Combustible gas detector. A portable hydrocarbon gas analyzer with associated sampling line and probe.

4.2.1 Safety. Certified as safe for operation in explosive atmospheres.

4.2.2 Range. Minimum range of 0-100 percent of the lower explosive limit (LEL) as propane.

4.2.3 Probe diameter. Sampling probe internal diameter of 0.625 cm (1/4 inch).

4.2.4 Probe length. Probe sampling line of sufficient length for easy maneuverability during testing.

4.2.5 Response time. Response time for full-scale deflection of less than 8 seconds for detector with sampling line and probe attached.

5. TEST PROCEDURE

5.1 Pressure. Place a pressure tap in the terminal, plant, or service station vapor control system, as close as possible to the connection with the truck tank. Record the pressure periodically during testing.

5.2 Calibration. Calibrate the combustible gas detector with 2.2 percent propane by volume in air for 100 percent LEL response.

5.3 Monitoring procedure. During loading or unloading, check the periphery of all potential sources of leakage of the truck tank and of the terminal, plant, or service station vapor collection system with a combustible gas detector.

5.3.1 Probe distance. The probe inlet shall be 2.5 cm from the potential leak source.

5.3.2 Probe movement. Move the probe slowly (2.0 cm/second). If there is any meter deflection at a potential leak source, move the probe to locate the point of highest meter response.

5.3.3 Probe position. As much as possible, the probe inlet shall be positioned in the path of (parallel to) the vapor flow from a leak.

5.3.4 Wind. Attempt as much as possible to block the wind from the area being monitored.

5.4 Recording. Record the highest detector reading and location for each incidence of leakage.

APPENDIX C

LEAK DETECTION PROCEDURE FOR BOTTOM-LOADED TRUCK TANKS BY BAG CAPTURE METHOD

1. PRINCIPLE

The volume of leakage from a truck tank during loading is measured directly by placing calibrated bags over all potential sources of leakage. This quantitative monitoring procedure is an enforcement tool to confirm the continuing existence of leak-tight conditions.

2. APPLICABILITY

This method is applicable to determining the leak-tightness of truck tanks during bottom-loading without taking the truck tank out of service. The method is applicable only if the vapor control system does not create back-pressure in excess of the pressure limits of the truck tank compliance leak test. This method cannot be applied to truck tanks during top-loading, vapor collection equipment on truck tanks, or vapor control systems at terminals, plants, or service stations.

3. DEFINITIONS

3.1 Truck tank. Any container, including associated pipes and fittings, that is used for the transport of gasoline.

3.2 Compartment. A liquid-tight division of a truck tank.

3.3 Truck tank vapor collection equipment. Any piping, hoses, and devices on the truck tank used to collect and route the gasoline vapors in the tank to the bulk terminal, bulk plant, or service station vapor control system.

3.4 Vapor control system. Any piping, hoses, equipment, and devices at the bulk terminal, bulk plant, or service station which is used to collect, store, and/or process gasoline vapors.

4. APPARATUS

4.1 Manometer. Liquid manometer, or equivalent, capable of measuring up to 6250 pascals (25 inches H_2O) gauge pressure with $\pm$ 25 pascals ($\pm$ 0.1 inches H_2O) precision.

4.2 Plastic bag. An air-tight bag, large enough to cover the truck tank's dome cover. One bag is needed for each compartment.

4.3 Bicycle tire. A bicycle innertube, or similar apparatus, modified to the appropriate diameter to fit over the truck tank's dome cover and lie flat on the top of the truck tank. One tire is needed for each compartment.

4.4 Dry gas meter.

4.5 Pump.

4.6 Calibration platform. A platform constructed such that air can be introduced through hole in the center of platform, and large enough for bicycle tire to lie flat on it.

5. BAG VOLUME CALIBRATION

5.1 Attach bag to innertube and seal with tape or other applicable sealant to ensure no leakage around interface.

5.2 Fill innertube with water.

5.3 Place bag apparatus on the calibration platform so that the air inlet is situated under the bag.

5.4 Remove air from bag.

5.5 Connect pump to dry gas meter and dry gas meter to inlet on the calibration platform.

5.6 Pump air into bag until bag is full. Record the volume from the dry gas meter and indicate volume on bag.

6. TEST PROCEDURE

6.1 Place a pressure tap in the terminal, plant, or service station vapor control system, as close as possible to the connection with the truck tank. Record the pressure periodically during testing.

6.2 During loadings, place a bag apparatus over the dome cover of each compartment in the truck tank being filled.

6.3 Remove air from bags.

6.4 Check to ensure there is a tight seal between the base of the bag apparatus and the top of the truck tank.

6.5 During loading, estimate volume of vapors collected in bags. If a bag fills before loading is complete, empty bag and resume testing.

6.6 Estimate total volume of vapors collected in the bags, making allowances in the volumes for tank domes or other equipment

6.7 Record capacity of truck tank.

6.8 Determine allowable volume of vapor leakage from truck tank as in Section 7.

6.9 Determine total loading time. This includes only time when filling is actually occurring, not breaks during the loading operation.

7. CALCULATIONS

7.1 Equation. The allowable volume of leakage from a truck tank can determined from equation 7-1.

$$V_L = (0.5V)\left(\frac{T}{t_p}\right)\left(1 - \frac{P_f}{P_i}\right) \qquad \text{(Equation 7-1)}$$

Where:
- V_L = allowable volume of leakage (liters)
- V = capacity volume of tank (liters)
- P_i = initial pressure for the compliance pressure test (absolute units)
- P_f = final pressure for the compliance pressure test (absolute units)
- t_p = time limit for pressure drop for the compliance pressure test (minutes)
- T = total time for loading (minutes)

7.2 Example. A 20,000 liter tank is filled to capacity in 10 minutes. The compliance pressure test has an allowable pressure drop in 5 minutes from 4500 pascals (18 inches H_2O gauge, 425 inches H_2O absolute) to 3750 pascals (15 inches H_2O gauge, 422 inches H_2O absolute). The allowable volume of leakage is 140 liters.

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16. ABSTRACT

This report provides the necessary guidance for development of regulations to limit emissions of volatile organic compounds (VOC) from gasoline tank trucks and vapor collection systems at bulk terminals, bulk plants and service stations. The intent of this guidance is to define leak tight conditions and related test procedures for vapor collection systems and tank trucks while loading and unloading gasoline at these facilities. The control approach described in this document is improved maintenance and would be enforced through the surveillance and periodic testing of leak points. This guidance includes a recommended regulation and testing procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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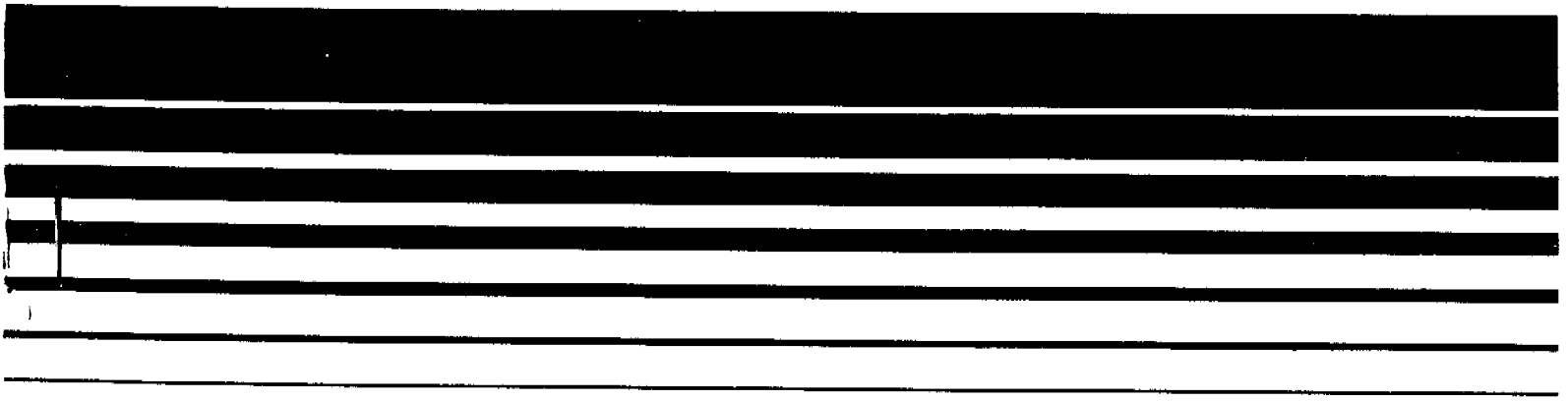
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Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products



APPENDIX B

VOC EMISSION CALCULATIONS

B.1 INTRODUCTION

The following methods have been developed to calculate the uncontrolled emissions from the following pharmaceutical process operations. These process operations are:

I. Charging

II. Evacuation (Depressuring)

III. Nitrogen or Air Sweep

IV. Heating

V. Gas Evolution

VI. Vacuum Distillation

VII. Drying

Some simplifying assumptions have been made; the general assumption for most of the following calculations is that the Ideal Gas Law applies. In applying these equations, it is important to use the correct number of operating hours for calculating daily or annual emission estimates.

Equation No. 1: $$n = \frac{PV}{RT}$$

where:
n = # of pound moles;
P = absolute pressure, in mm Hg;
V = volume, in $ft.^3$;
T = temperature, in ^oK; ($^oK = {}^oC + 273$)
R = gas law constant, 999 $\left(\frac{ft^3 \text{ mm Hg}}{{}^oK \text{ lb moles}}\right)$

The Ideal Gas Law is used to calculate the lbs/hr of VOC emitted, as follows:

Equation No. 2: $$Se = \frac{Pi\ (Xi)\ Vr\ (MWi)}{RT}$$

where:
Se = lbs/hr of VOC emitted;
Pi = vapor pressure of VOC at T, in mm Hg;
Xi = mole fraction of VOC in liquid mix;
Vr = rate of displacement, in ft^3/hr;

$R = 999 \frac{\text{mm Hg ft}^3}{\text{lb mole } ^\circ\text{K}}$

T = temperature in $^\circ$K;

MWi = molecular weight of VOC, in lbs/lb mole.

The mole fraction, Xi, above must be included in the case of a liquid mix. Mole fraction is calculated as follows:

Equation No. 3:

$$Xi = \frac{\text{moles of i in liquid mix}}{\text{total moles of liquid mix}}$$

where: Xi = mole fraction of i;
i = denotes the VOC in question

For one component systems, Xi = 1.

The vapor pressure, Pi, is calculated using Antoine's equation or taken from tables of vapor pressure.

Equation No. 4:

$$\text{Log}_{10}Pi = a - \left(\frac{b}{c+Ti}\right)$$

where: Pi = vapor pressure of the VOC (mm Hg);
Ti = temperature of the air containing the VOC vapor ($^\circ$C);
a,b,c = Antoine's equation constants.[1] See Lange's Handbook of Chemistry

Vapor Pressure Tables

Vapor pressures from Perry's[2] are interpolated or extrapolated using a Cox chart. An example is included as Figure 4-1.

B.2 METHODS AND CALCULATIONS

I. Charging

This method can be used to calculate emissions from a vessel containing a liquid VOC when a liquid is charged into the vessel.

Assumptions - The volume of gas displaced from the vessel is equal to the volume of liquid charged into the vessel. The air displaced from the vessel is saturated with the VOC vapor at the exit temperature. (Note: if data are available to calculate concentration, then this can be used in place of saturation.)

Calculations -

1. Calculate the rate of air displacement in ft^3/hr:

Equation No. 5: $$Vr = Lr\ (0.134\ ft^3/gal)\ (60\ \frac{min}{hr})$$

where: Vr = the rate of air displacement, in ft^3/hr;
Lr = liquid pumping rate, in gpm.

2. Determine the mole fraction of each VOC in the vessel during the pumping, Xi, using Equation No. 3.
3. Calculate the vapor pressure of each pure VOC, Pi, using Equation No. 4.
4. Calculate the lbs/hr of each VOC emitted, Se, using Equation No. 2.

II. Evacuation (Depressuring)

This method is used to calculate emissions from the evacuation (or depressuring) of any vessel containing a VOC and a "noncondensable." Usually the vessel will be a still and the "noncondensable" will be air or nitrogen.

Assumptions - The absolute pressure in the vessel decreases linearly with time. There is no air leakage into the vessel. The composition of the VOC mix does not change during the evacuation (or depressuring) and there is no temperature change. The air displaced is saturated with the VOC vapor at the vessel temperature.

Calculations -

1. Calculate the mole fraction,Xi, for each VOC in solution using Equation No. 3.
2. Calculate the vapor pressure,Pi , of each VOC at the vessel temperature using Equation No. 4.
3. Calculate the initial volume of the air in the vessel:

$$Vi = \left[\frac{Pa - \Sigma(PiXi)}{760}\right] F_s$$

where: Vi = the initial air volume in the vessel, ft^3 (standard);

$\Sigma (PiXi)$ = the sum of the products of the vapor pressures and the mole fractions of each VOC in the solution;

Pa_1 = initial pressure, in mmHg,

760 = atmospheric pressure, in mmHg.

F_s = free space in the still, in $ft.^3$

4. Calculate the final air volume in the vessel:

$$V_f = \left[\frac{Pa_2 - \Sigma (PiXi)}{760}\right] F_s$$

V_f = the final air volume in vessel, in ft^3 (standard);

where: Pa_2 = final air pressure in the vessel, mmHg.

5. Calculate the rate of air removal from the vessel:

$$Vr = \frac{Vi - Vf}{t}$$

where: Vr = the rate of air removal from the vessel, in ft^3/hr;

t = time of evacuation of vessel, in hrs.

6. Calculate initial ratio of air to total VOC vapor:

$$Ri = \frac{760 - \Sigma (PiXi)}{\Sigma (PiXi)}$$

where: $Ri = \frac{\text{moles air}}{\text{moles VOC}}$

7. Calculate final ratio of moles air to moles total VOC vapor:

$$R_f = \frac{Pa_2 - \Sigma (PiXi)}{\Sigma (PiXi)}$$

where: $R_f = \frac{\text{moles air}}{\text{moles VOC}}$

8. Calculate the average ratio of moles air to moles total VOC vapor:

$$Ra = \frac{Ri + Rf}{2}$$

9. Calculate volume of total VOC vapor discharged, ft^3/hr:

$$VRS = \frac{Vr}{Ra}$$

where: VRS = VOC emission from the system, ft^3/hr.

10. Calculate the emission rate, Se, for each VOC in lbs/hr using Equation No. 2 substituting VRS for Vr and use pressure of one atmosphere.

III. Nitrogen or Air Sweep

This method is used to calculate emissions when nitrogen, air, or other "noncondensable" is used to purge or sweep a vessel or other device.

Assumptions - The nitrogen gas exiting the vessel is saturated with VOC vapor at the exit temperature.

Calculations -

1. Calculate the rate of nitrogen sweep in ft^3/hr:

Equation No. 6: $$Vr_1 = Ns \times 60 \text{ min/hr}$$

where: Vr_1 = the rate of nitrogen sweep in ft^3/hr, standard;

Ns = the rate of nitrogen sweep in ft^3/min, standard.

2. Calculate the mole fraction, Xi, for each VOC using Equation No. 3.

3. Calculate the vapor pressure, Pi, for each VOC at the exit temperature using Equation No. 4.

4. Calculate the rate of total gas displaced from the vessel, ft^3/hr.

Equation No. 7:
$$Vr_2 = Vr_1 \left[\frac{760}{760 - \Sigma(PiXi)}\right]$$

where: Vr_2 = rate of gas displaced from vessel, in ft^3/hr, standard;

Vr_1 = rate of nitrogen sweep, in ft^3/hr;

$\Sigma(PiXi)$ = the sum of the products of the vapor pressures and mole fractions for each VOC;

760 = vapor pressure of nitrogen sweep , in mmHg.

5. Calculate the rate of VOC emission in lbs/hr, Se, for each VOC using Equation No. 2 substituting Vr_2 for Vr.

IV. Heating

This method is used to calculate the emissions from the heating of a still containing a VOC and a "noncondensable," usually air.

Assumptions - The moles of air displaced from the still are a result of (1) the expansion of air upon heating and (2) an increase in VOC vapor pressure. The moles of air displaced from the receiver are equal to the moles of air displaced from the still. The air displaced from the receiver is saturated with VOC vapor in equilibrium with the VOC mixture in the receiver at the temperature of the receiver.

Calculations -

1. Calculate the mole fraction, Xi, for each VOC in the still using Equation No. 3.
2. Calculate the vapor pressure, Pi, of each pure VOC at the initial temperature (T_1) using Equation No. 4.
3. Calculate the initial pressure of the air in the still:

Equation No. 8: $$Pa_1 = 760 - \Sigma(PiXi)_{T_1}$$

where: Pa_1 = the initial air pressure in the still in mmHg ;

$\Sigma(PiXi)_{T_1}$ = the sum of the products of the vapor pressures and the mole fractions of each VOC at the initial temperature;

760 = atmospheric pressure, in mmHg.

4. Calculate the vapor pressure, Pi, of each pure VOC at the final temperature (T_2) using Equation No. 4.
5. Calculate the final pressure of air in the still:

Equation No. 9: $$Pa_2 = 760 - \Sigma(PiXi)_{T_2}$$

where: Pa_2 = final air pressure in the still, in mmHg;

$\Sigma(PiXi)_{T_2}$ = sum of the products of the vapor pressures and the mole fractions for each VOC at the final temperature;

760 = atmospheric pressure, in mmHg.

6. Calculate the moles of air displaced to the receiver (and to the environment):

Equation No. 10:

$$(n_1-n_2) = \frac{V}{R}\left(\frac{Pa_1}{T_1} - \frac{Pa_2}{T_2}\right)$$

where:

(n_1-n_2) = number of lb moles of air displaced to the receiver;

V = volume of free space in still, in $ft.^3$;

R = gas law constant, 999 $\frac{mm\ Hg\ ft^3}{lb\ moles\ ^oK}$

Pa_1 = initial air pressure in still, in. mmHg;

Pa_2 = final air pressure in still, in. mmHg;

T_1 = initial temperature in still, in. ^oK;

T_2 = final temperature in still, in. ^oK.

7. Calculate the number of lb moles of VOC vapor displaced:

$$ns = \frac{\Sigma(PiXi)_{TR}}{760 - \Sigma(PiXi)_{TR}}\ (n_1 - n_2)$$

where:

ns = pound moles of VOC vapor displaced from the receiver;

$\Sigma(PiXi)_{TR}$ = sum of products of vapor pressures and mole fractions for each VOC at the temperature of the receiver.

8. Calculate the lbs of each VOC vapor emitted, Se:

Equation No. 11:

$$(Se)_i = (n_s)\ MW_{si}\ (X_i)$$

where:

$(Se)_i$ = lbs of VOC (i) vapor emitted;

n_s = number of lb moles of all VOC vapor emitted;

MW_{si} = molecular weight of VOC (i);

X_i = mole fraction of VOC (i) in the vapor.

V. Gas Evolution

This method is used to calculate emissions when a gas is generated as the result of a chemical reaction. The gas comes into contact with one or more VOC, usually solvents, and is saturated.

Assumptions - The gas is saturated with VOC vapor at the exit temperature.

Calculations -

1. Determine the rate of gas evolution, Wg, in lbs/hr, from the stoichiometry of the chemical reaction, and the reaction time.
2. Calculate the rate of gas evolution in ft^3/hr:

Equation No. 12:

$$Vr_1 = \frac{Wg\ RT}{P\ MWg}$$

where:

Vr_1 = the rate of gas evolution, in ft^3/hr;

R = the gas law constant, 1.314 $\frac{atm\ ft^3}{lb\ mole\ ^oK}$

T = the temperature at the exit, in ^oK (^oC + 273);

Wg = the rate of gas evolution, in lbs/hr;

P = the pressure in the vessel, in. atm.;

MWg = the molecular weight of the gas, in lb/lb mole.

3. Calculate the mole fractions, Xi, of the VOC in solution using Equation No. 3.
4. Calculate the vapor pressures, Pi, of the pure VOC at the exit temperature using Equation No. 4.
5. Calculate the rate of gas displacement in ft^3/hr:

Equation No. 13:

$$Vr_2 = Vr_1 \left[\frac{760}{760 \times \Sigma(PiXi)}\right]$$

where:

Vr_2 = rate of gas displacement, in ft^3/hr;

Vr_1 = rate of gas evolution, in ft^3/hr;

760 = atmospheric pressure, in mmHg;

$\Sigma(PiXi)$ = the sum of the products of the vapor pressure and the mole fraction of each VOC at the exit temperature.

6. Calculate the VOC emission rate, Se, in lbs/hr using Equation No. 2.

VI. Vacuum Operations

This method is used to calculate emissions from vacuum operations. Air leaks into the system and becomes saturated with the VOC vapor at the receiver temperature and is subsequently discharged by the jet to the atmosphere.

The air leak rate is best determined by closing off the jet from the still, condenser, and receiver and noting the rise in absolute pressure over a short period of time. The air leak rate can then be calculated using Equation No. 14 below. Maximum air leakage has also been estimated for "commercially tight systems" for various system volumes and pressures.[3]

Assumptions - The air that leaves the system is saturated with solvent vapor at the receiver temperature.

Calculations -

1. Calculate the air leak rate into the system:

Equation No. 14:

$$Vr_1 = \frac{273\ Fs}{Tt}\left(\frac{P_2 - P_1}{760}\right)$$

where:

Vr_1 = air leak rate, in ft^3/hr (standard);
Fs = total free space under vacuum, in $ft.^3$;
P_1 = absolute pressure at start of test, in mmHg;
P_2 = absolute pressure at end of test, in mmHg;
t = time of test, in hrs;
T = temperature of still, in ^oK;
273 = temperature at standard conditions, in ^oK.

2. Calculate the rate of VOC emissions, lbs/hr:

Equation No. 15:

$$Se = MWs\ \frac{Vr_1}{359}\left(\frac{P\ system}{P\ system - Ps} - 1\right)$$

where:

Se = rate of VOC emission, in lbs/hr;
P system = absolute pressure of receiver, in mmHg;
Ps = vapor pressure of the VOC at the receiver temperature, in mmHg;
MWs = molecular weight of VOC, in lb/lb mole;
359 = the volume that 1 lb mole of gas occupies at standard conditions, in $ft.^3$.

3. If leak rate is obtained in lbs/hr from reference 3, calculate VOC emission lbs/hr:

Equation No. 16:

$$Se = \frac{La\ MWs}{29}\left(\frac{P\ system}{P\ system - Ps} - 1\right)$$

where: La = leak of air into the systems, in lb/hr;
29 = molecular weight of air, in lb/lb mole.

VII. Drying

This method is used to calculate VOC emissions from either batch or continuous drying operations. Although it is possible to determine emissions from an analysis of the dryer off-gas, it is usually simpler and more accurate to use a material balance.

Assumptions - Samples of the product before and after the dryer are analyzed for VOC content.

Calculations -

1. Calculate the rate of VOC emissions, lbs/hr:

Equation No. 17:

$$Se = \frac{B}{t}\left(\frac{PS_1}{100 - PS_1} - \frac{PS_2}{100 - PS_2}\right)$$

where: Se = rate of VOC emission, lbs/hr;
B = weight of batch (dry), lbs;
t = time of drying operation, hrs;
PS_1 = percent of VOC in wet material into dryer;
PS_2 = percent of VOC in less wet material from dryer.

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PREFACE

Emphasis on the control of volatile organic compounds through the State Implementation Plans, new source performance standards, and national emission standards for hazardous air pollutants has created a need for standardized test procedures. In setting national performance standards for new sources and national emission standards for hazardous air pollutants, the Environmental Protection Agency has followed a policy of establishing a reference method for each regulated source category and pollutant. Under the State Implementation Plan process, however, test methods and erocedures are defined by the States. Thus, the case-by-case approach used by the Environmental Protection Agency for national standards could conflict with State established methods. In addition, the case-by-case approach does not provide sufficient guidance to the States in their efforts to develop regulations for a large number of sources and organic compounds.

The purpose of this document, therefore, is to provide guidance to the States on the measurement of volatile organic compounds from a diversity of sources and pollutants that is consistent with the methodology being applied by the Environmental Protection Agency as it develops regulations for specific sources and pollutants.

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METHODS FOR DETERMINING VOLATILE ORGANIC COMPOUNDS AS CARBON IN STATIONARY SOURCES

Introduction

Volatile organic compound (VOC) emission control regulations are being developed by EPA and by State and local agencies to meet the oxidant control needs. In some cases, the regulations are in terms of the volatile organic content of solvents. In other cases, they cover organic volume or mass concentrations, mass emission rates, and control equipment efficiencies. Regardless of the approach taken in the regulation, consideration must be given to the expression of emission limits in terms of what can be measured, and to the cost and practicality of the test methods.

One concept of volatile organic emission measurement is the determination of organic carbon mass concentration. The rationale for selecting this concept and conceptual approach for writing regulations in terms of volatile organic carbon are discussed herein, and two specific test methods are presented to implement the recommended approach.

Rationale for Selecting Organic Carbon

In considering volatile organic compound test methods one must recognize that organic emissions normally consist of a mixture of compounds and that there is presently no detection technique having an inherent, quantitative response to the total molecular structure of the mixture. Several detection techniques respond to organic compounds; however, the response can vary widely from compound to compound and may, therefore, not be proportional to the total organic mass or volume in a mixture.

Such is the case of the flame ionization detector (FID), the most commonly used detector for organic measurements. The FID response can vary from compound to compound because it is a function of the number of carbon atoms, the type of bonds, and the elements present in the organic molecules. Thus, if the volatile organic emission limit is expressed in terms that require the measurement of the total molecular structure of the organic emissions, the variable response of the flame ionization detector must be overcome by one of the methods described below.

1. Gas Chromatograph/Flame Ionization Detector. This method involves the separation of the organic components into discrete compounds using gas chromatography (GC). The compounds are identified, and the FID is calibrated for each of the identified compounds. The compounds are then measured individually, and the total mass concentration is determined by adding the individual mass concentration values; methane can be identified and excluded from the results. This method may be eractical where only two or three compounds are emitted, such as in maleic anhydride plants; but if it is applied to sources that emit numerous organics, the time and expense would be formidable. For example, over 20 peaks were noted in a preliminary study of emissions from the manufacture of nitrobenzene.

2. Direct Flame Ionization Detector with Emission Stream Characterization. This method involves direct measurement with an FID analyzer,

with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic components in the stream. If present, methane will, of course, also be measured.

In practice, this method can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) where only one compound is known to exist, (2) when the organic compounds consist of only hydrogen and carbon, (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and only the relative concentrations are to be assessed, or (5) where the FID can be calibrated against mass standards of the emissions (solvent emissions, for example).

In the case of volatile organic solvents, accurate measurements by direct FID analyzers without calibration with solvent standards are seldom possible because these solvents are often a mixture of multiple unknown compounds. Even if the emissions can be separated and identified using a GC, accurate determination of the average FID response is often impractical. In addition, the emissions may be altered as they pass through a control device: for example, they may be partially oxidized in an incinerator or selectively retained in an adsorber. In such cases the measurement is more difficult and cannot be corrected with

methods are normally characterized by portability of equipment, procedural simplicity, and low cost. Methods based on thermal conductivity or low-cost portable FID analyzers would be candidates for approval as screening methods.

Recommended Reference Method

A reference method that involves indirect measurement of volatile organic carbon by an oxidation-reduction is recommended. This necessitates that the emission limits be expressed in terms of organic carbon. If the emission limits and a universal reference method are both based on organic carbon, the volatile organic standard will be expressed in clear, unambiguous terms. No other known practical test method could accomplish this objective for a wide range of volatile organic compounds.

A draft "Reference Method for Determination of Total Gaseous Nonmethane Organic Emissions as Carbon" is included as Attachment 1. The method requires a system for separating total nonmethane organics from other carbon compounds, converting the total nonmethane organics to methane, and analysis of the methane by a flame ionization detector. Other than requiring this general equipment, the method provides performance specifications designed to assure correct performance of the separation-detection system. Depending on the organic carbon concentration, the method may allow the use of the NDIR to detect the CO_2 formed by the initial oxidation step.

The concept upon which the method is based has been utilized for many years in Los Angeles County, where it has been demonstrated to be valid and effective for compliance determinations.

There is at least one private laboratory that is able to perform the analysis on a fee basis. The oxidation-reduction analysis concept for measurement of gaseous nonmethane organic compounds is also offered commercially by at least one instrument vendor. Although the availability of instruments is admittedly very limited, there is no serious technical impediment that would prevent additional vendors from designing and producing acceptable instruments.

Because of the somewhat limited use potential for the Los Angeles laboratory-oriented procedure and the present limited production of commerical instruments for field use, the OAQPS recommendation of the oxidation-reduction reference method for the definition of organic emissions is recognized as leading the technology. Wide acceptance of the organic carbon reference method will, however, provide the needed inducement for additional vendors to enter the market and thereby increase the supply and variety of organic carbon analysis instruments.

A draft of the Los Angeles procedure is included as Attachment 2. Although the detail is considerable, some agencies may wish to assemble the laboratory apparatus. The Emission Measurement Branch of OAQPS is working to refine the operating details of the procedure; as information becomes available, it will be incorporated into the method.

Alternate Methods

An "Alternate method" may have only limited applicability or other deficiencies that prevent its designation as a reference method. Such methods may offer practical advantages and produce results adequate for determining compliance in certain applications. Where such methods are applicable, the results may be accepted in lieu of reference method results.

As a specific example, methods based on direct measurement with flame ionization detectors are often practical for hydrocarbon compounds, and, in addition, the equipment is widely available. An FID analyzer will be less costly and may be less complicated for field application that an oxidation-reduction analyzer; therefore, for those applications where such methods can be made to produce accurate results, approval of them as alternate methods is desirable.

The Office of Air Quality Planning and Standards, EPA,has drafted an "Alternate Test Method for Direct Measurement of Total Gaseous Organic Compounds Using a Flame Ionization Detector," which is included as Attachment 3. This method outlines the known characteristics and limitations of FID techniques and provides procedures needed to assure its proper operation. The method does not and is not intended to indicate specific applications where the method can (or cannot) be used or correction factors to be applied to the results. Such determinations must be made on a case-by-case basis founded on knowledge of

the contents of the stream under test and the limitations of the detector.

Screening Methods

In addition to the limitations associated with alternate methods, screening methods may also lack precision. In spite of such shortcomings, screening methods may play an important role in any volatile organic control program. As a practical matter, the cost of applying a reference or alternate method to all or even a majority of the regulated effluent streams in a jurisdiction may be unreasonable; therefore, less expensive, simpler testing techniques will be needed.

To date, OAQPS has made effective use of an explosimeter to detect vapor leaks in gasoline marketing operations. In addition, an inexpensive hydrocarbon monitor using a solid-state ionization detector was designed by OAQPS and has been used successfully as an emissions breakthrough detector on the exit of a carbon adsorber. More recently, OAQPS has initiated a test program associated with the development of new source standards, using portable analyzers to detect leaks occurring in unit operations in the petroleum industry. Two analyzers will be employed in this program, one involving a combustion/thermal-conductivity-type detector and the other a low-cost FID.

Another example of a screening method would be the case of an FID analyzer applied to an unknown gas stream. In such case there is often enough information available to provide a rough estimate of the analyzer accuracy, but a more exact determination would be prohibitive. In such an

event the FID may be used as an alternative method for determining compliance, provided that sufficient buffer is included to account for the possible inaccuracy.

Regulatory Language

Examples of how general regulations may be expressed in terms of the reference method that measures organic carbon concentration are as follows:

1. To regulate concentration:

   "Emissions of organic carbon shall not exceed _____ grams carbon per cubic meter."

2. To regulate mass rate:

   "Emissions of organic carbon shall not exceed _____ grams carbon per hour" or "Emissions of organic carbon shall not exceed _____grams carbon per kilogram of solvent used."

To protect the analytical instrument from contamination from particulates and condensation, a filter and heated sample line (temperature defined) must also be included in the emission regulations.

ATTACHMENT 1. REFERENCE METHOD FOR DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON--AUTOMATED ANALYZER VERSION

1. Principle and Applicability

1.1 Principle. Conditioned stack gas is transported to and analyzed by a semiportable gas chromatograph (GC) equipped with a flame ionization detector (FID). The total gaseous nonmethane organic (TGNMO) fraction is separated by means of various GC columns from the other constituents, oxidized to CO_2 and then reduced to methane (CH_4) before it is introduced to the FID. In this manner, the variable response of the FID associated with different types of organics is eliminated, and a count of TGNMO carbon atoms is obtained.

1.2 Applicability. The method is applicable to the semicontinuous measurement of total gaseous nonmethane organics in source emissions.

2. Range and Sensitivity

2.1 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

None.

4. Apparatus

4.1 TGNMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory. The

primary components of the analyzer are an FID preceded by a GC column to achieve the necessary separation of TGNMO from other carbon compounds. Oxidation and reduction catalysts then convert the TGNMO to CH_4 prior to detection. The analyzer shall be accompanied by an instruction manual (supplied by the manufacturer if the analyzer was commercially produced) describing proper operation and maintenance procedures. In addition to the specific procedures required by this method, the analyzer shall be demonstrated prior to initial use to be capable of proper separation, oxidation, and reduction. As a minimum this demonstration shall include measurement of a known TGNMO concentration present in a mixture that also contains similar amounts of CH_4, CO_2, and CO. Certification of such demonstration by the manufacturer is acceptable.

4.2 Sample Conditioning or Interface System (see Figure 1). Probe with filter, 6.4 mm O.D. Teflon[1] sample line, Teflon-coated diaphragm pump, and Teflon flow control valves. A heating system capable of maintaining all components at 120°C or greater shall be included. The pump shall be sized so that the sample residence time from the probe to the instrument will not exceed 15 seconds.

4.3 Potentiometric Recorder (optional). Strip chart recorder with a voltage output compatible with the analyzer.

5. Reagents

5.1 Combustion Gas. Air containing less than 2 ppm organics (methane or carbon equivalent).

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[1]Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

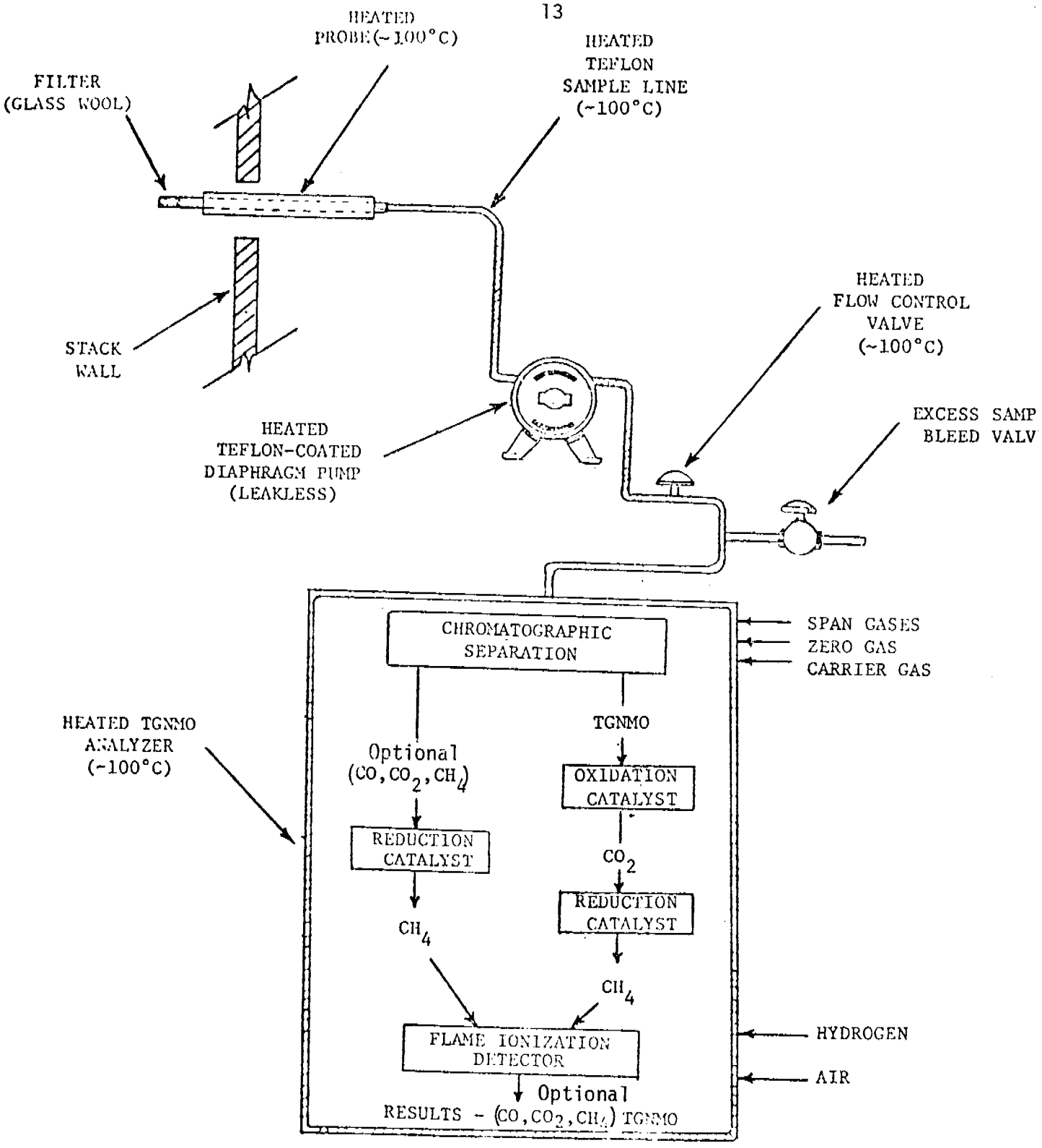


FIGURE 1. On-site Application of TGNMO Analyzer

7.1.4 Begin Actual Sampling. Set the signal attenuation to yield a minimum response of 10 percent of full scale, unless the stack concentration is less than 1 ppm. Adjust the flow and bleed valves to minimize sample line residence time. Perform the analysis a minimum of four times. Report the average of the final four readings. The analyzer cycle time is normally 10 to 15 minutes.

7.1.5 At the conclusion of the sampling tests, but at least once every day, introduce zero and span gas to the analyzer to determine zero and span drifts. If the analyzer has drifted beyond the allowable performance specification, the tests shall be considered invalid.

7.2 Calibration

7.2.1 Calibration Curve. Maintain a record of performance of each item. Determine the linearity of the analyzer for TGNMO as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respectivezeroing controls to indicate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these two steps until adjustments are no longer necessary. Calculate a predicted response for the 5-10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If this value is not within ± 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any event, this linearity performance specification shall be met before the analyzer is placed in actual use.

7.3 Catalyst Performance Check. These checks should be performed on a frequency established by the amount of use of the analyzer, and the nature of the organic emissions to which it is exposed. To confirm that the oxidation catalyst is functioning in the correct manner, the operator must turn off or bypass the reduction catalyst while operating the analyzer in an otherwise normal fashion. If oxidation is adequate, the only gas that will then reach the detector will be CO_2, to which the FID has no response. If responses are noted, then the oxidation catalyst must be replaced. To confirm the operation of the reduction catalyst, reverse the above procedure. If CO_2 in the calibration gases is not reduced to CH_4 as it should be, then the reduction catalyst must be replaced.

8. Calculations

8.1 Determine concentrations of TGNMO (propane equivalent) directly from the calibration curves. Multiply this number by 3 to obtain ppm TGNMO (methane or carbon equivalent).

8.2 Conversion to mass concentration values for TGNMO as carbon is made as follows:

mg TGNMO/m^3 as carbon = ppm TGNMO (methane or carbon equivalent)

x 0.499

where:

$$1 \text{ ppm TGNMO (methane or carbon equivalent)} = \frac{1}{10^6} \times \frac{41.57 \text{ g-mole}}{m^3}$$

$$\times \frac{12000 \text{ mg}}{\text{g-mole}} = 0.499 \text{ mg/m}^3 \text{ as carbon.}$$

where:

Molecular weight of carbon = 12

Standard conditions: 20°C, 1 atm.

9. References

9.1 Albert E. Salo, Samuel Whitz, and Robert D. MacPhee. "Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared With Flame Ionization Detectors." Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Ma. Paper No. 75-33.2. June 15-20, 1975.

9.2 Instruction Manual, Byron Model 401 Total Emission Analyzer, Byron Instruments, Inc., 520 1/2 S. Harrington Street, Raleigh, N.C. 27601.

ATTACHMENT 2. DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON: MANUAL SAMPLING AND ANALYSIS PROCEDURE

1. Principle and Applicability

1.1 Principle. An emission sample is anisokinetically drawn from the stack through a heated filter and a chilled condensate trap by means of an evacuated gas collection tank. Total gaseous non-methane organics (TGNMO) are determined by combining the analytical results obtained from independent analyses of the condensate trap and evacuated tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide which is quantitatively collected in an evacuated vessel; a portion of the carbon dioxide is reduced to methane and measured by a flame ionization detector (FID). A portion of the sample collected in the gas sampling tank is injected into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide, carbon dioxide and methane; the nonmethane organics are oxidized to carbon dioxide, reduced to methane, and measured by a FID.

1.2 Applicability. This method is applicable to the measurement of total gaseous nonmethane organics in source emissions.

2. Apparatus

2.1 General. TGNMO sampling equipment can be constructed by a laboratory from commercially available components and

components fabricated in a machine shop. The primary components of the sampling system are a heated filter, condensate trap, flow control system, and gas sampling tank. (Figure 1). The primary components of the analytical system are an oxidation system for recovery of the sample from the condensate trap and a TGNMO analyzer. The TGNMO analyzer is a FID preceded by an oxidation catalyst, a reduction catalyst, and a GC column with backflush capability (Figure 2). The system for the removal and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, Non-Dispersive Infrared (NDIR) analyzer and an intermediate gas collection tank (Figure 3).

2.2 Sampling.

2.2.1 Probe. 1/8" stainless steel tubing heated to approximately 120°C.

2.2.2 Filter Holder. Stainless steel with a stainless steel or glass frit filter support and a Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached at the outlet of the probe.

2.2.3 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120 $\pm$ 14°C (248 $\pm$ 25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. A temperature gauge capable of measuring temperature to within

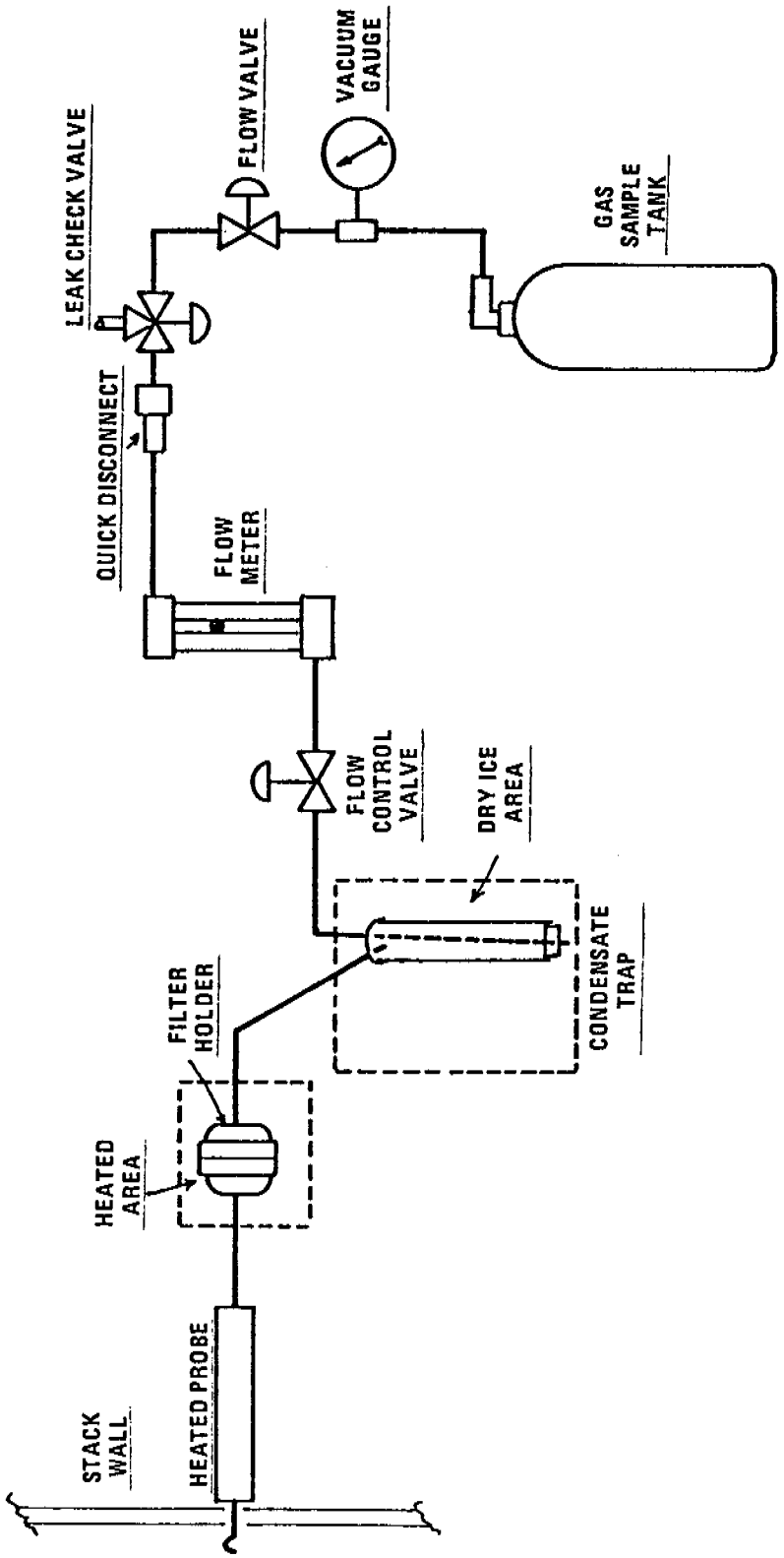


Figure 1. SAMPLING APPARATUS

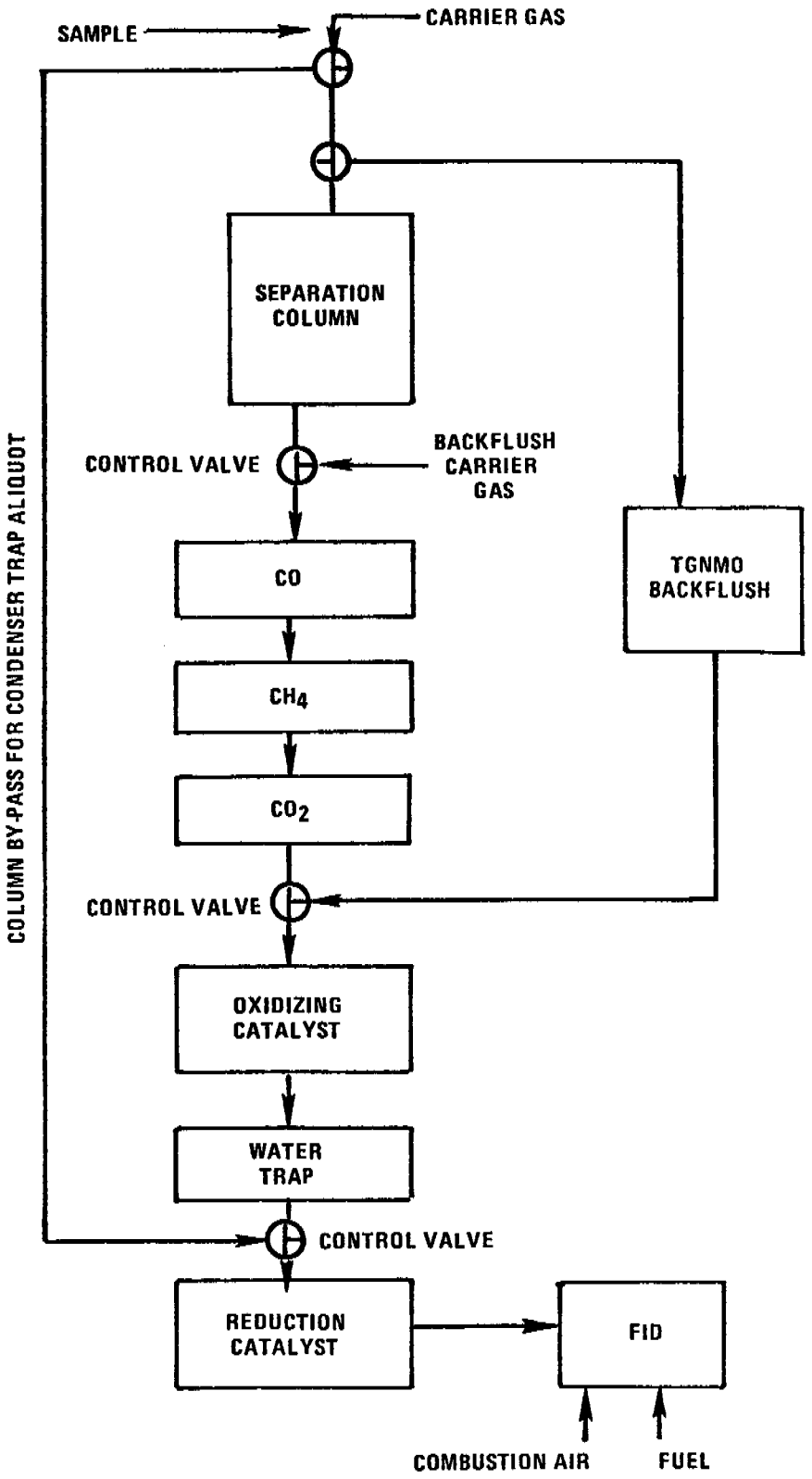
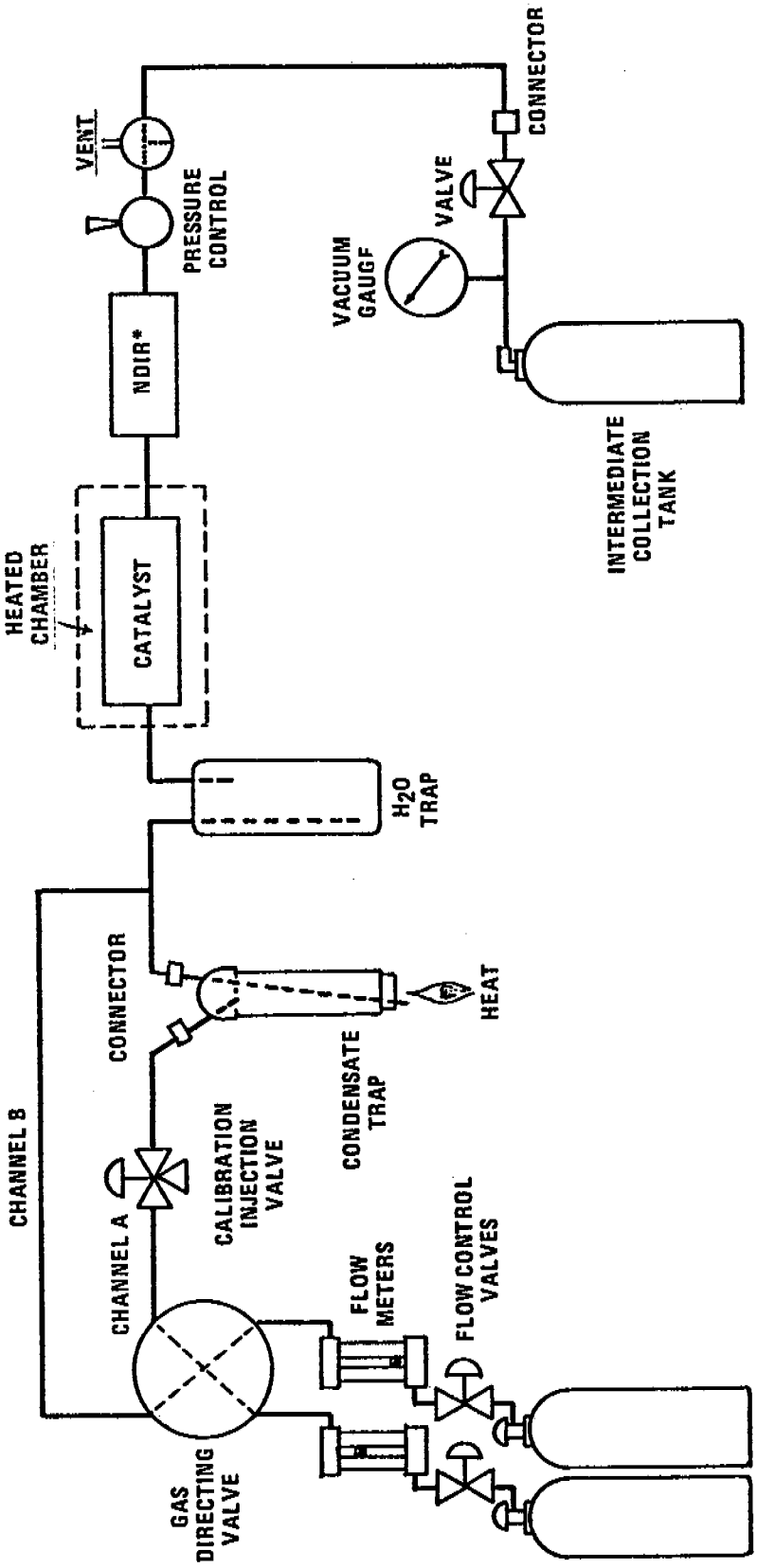


Figure 2. TOTAL GASEOUS NONMETHANE ORGANIC (TGNMO) ANALYZER SCHEMATIC



*FOR MONITORING PROGRESS OF COMBUSTION ONLY

Figure 3. CONDENSATE RECOVERY AND CONDITIONING APPARATUS

3° C (5.4° F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

2.2.4 Condensate Trap. The condensate trap shall be constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 4.

2.2.5 Flow Control System.

2.2.5.1 Needle Valve. To regulate sample gas flow rate.

2.2.5.2 Rate Meter. Rotameter, or equivalent capable of measuring flow rate to within ± 10 percent of the selected flow rate of about 80 cc/min. Other flow control systems capable of maintaining a constant sample rate of 80 cc/min ± 10 percent may be used subject to the approval of the Administrator.

2.2.6 Gas Collection Tank. Stainless steel or aluminum tank with a minimum volume of 6 liters. The tank is fitted with a vacuum gauge, a leakless valve, and a t-connector for conducting leak checks.

2.3 Analysis. For analysis, the following equipment is needed.

2.3.1 Condensate Recovery and Conditioning Apparatus (Figure 3).

2.3.1.1 Heat Source. A heat source sufficient to heat the condensate trap to a "cherry red" color. An electric muffle-type furnace or bunsen burner may be used.

2.3.1.2 Oxidizing Catalyst. A platinum and quartz catalyst constructed from a 44-inch length of 1/4" tubing of

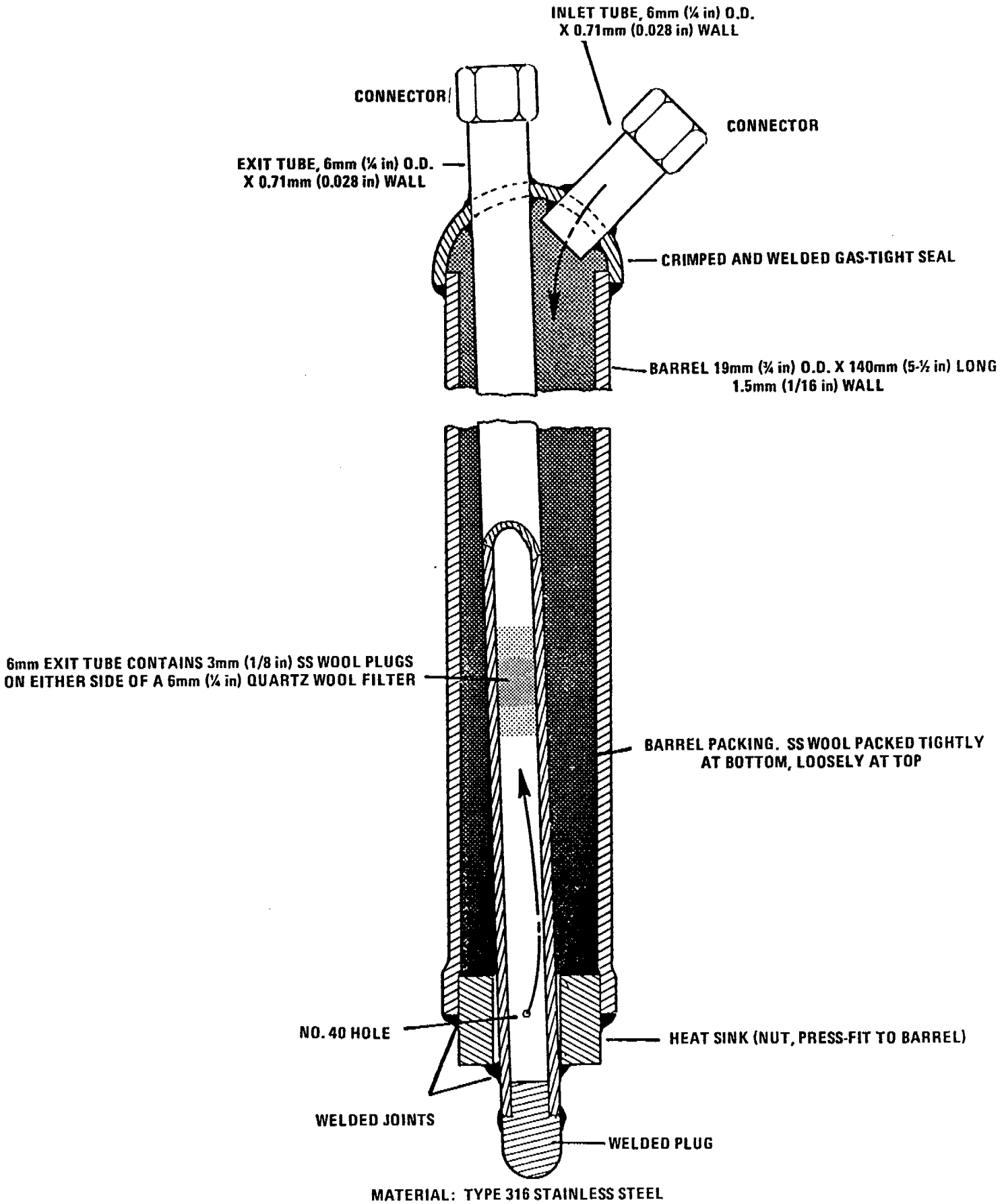


Figure 4. CONDENSATE TRAP[2]

70 percent Ni-30 percent Cr alloy packed as follows:

First 4 inches--empty.

Next 4 inches--8-10 mesh alumina coated with 0.5 percent finely divided platinum.

Next 28 inches--8 mesh quartz chips.

Last 8 inches--8-10 mesh alumina 0.5 percent platinum coated.

Other catalyst systems capable of meeting the catalyst efficiency criteria of this method (Section 4.4.2) may be used subject to the approval of the Administrator.

2.3.1.3 Water Trap. Any leak proof moisture trap capable of removing moisture from the gas stream may be used. A condensate trap designed according to the specifications of Figure 4 without packing in the exit tube will suffice.

2.3.1.4 NDIR Detector. Detector capable of indicating the CO_2 level in the zero to five percent range; required to monitor the combustion progress of the organic matter in the condensate trap.

2.3.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the NDIR detector at a constant pressure.

2.3.1.6 Intermediate Collection Tank. Stainless steel or aluminum collection vessel. Tanks with nominal volumes of 2 and 6 liters are recommended. The end of the tank is fitted with a t-connector, vacuum gauge, and leakless valve.

2.3.1.7 Calibration Injection Port. Injection port valve and sample loop for injection of calibration standards required

to check the combustion efficiency of the condensate recovery system.

2.3.2 Total Gaseous Nonmethane Organic (TGNMO) Analyzer. Semicontinuous GC/FID analyzer capable of: (1) separating CO, CO_2, CH_4, and gaseous nonmethane organics, (2) oxidizing the nonmethane organic fraction to CO_2, reducing the CO_2 to methane, and quantifying the methane. The analyzer shall be demonstrated prior to initial use to be capable of proper separation, oxidation, reduction, and measurement. As a minimum, this demonstration shall include measurement of a known TGNMO concentration present in a mixture that also contains CH_4, CO, and CO_2. (see paragraph 4.4.1) In addition, the analyzer shall meet the following performance specifications:

2.3.2.1 Linearity. $\pm$ 5 percent of the expected value for each full scale setting up to the maximum percent absolute (methane or carbon equivalent) calibration point. The analyzer shall be demonstrated prior to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 40,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 4.4.1.1) must be made before each use.

2.3.2.2 Zero Drift. One percent full scale per analysis of an emission test series.

2.3.2.3 Span Drift. One percent full scale per analysis of an emission test series.

2.3.2.4 The following components have been found to be acceptable for use in the TGNMO System:

2.3.2.4.1 Oxidation Catalyst. Type 316 stainless steel 0.25 inch OD tubing x 14 inches long packed with Hopcalite[1] 25 - 30 mesh; operated at 850° C.

2.3.2.4.2 Reduction Catalyst. Type 316 stainless steel 0.25 inch OD tubing x 7 inches long packed with 10 percent nickel on chromasorb W, 60-80 mesh; operated at 400° C. Method of preparation: 100 grams chromasorb W, 10 grams nickelous nitrate, 75 ml water, evaporated to dryness then heated in air for 4 hours to convert to nickel oxide. After packing the tubing, reduce overnight at 450° C and 30 ml/min H_2 to nickel metal.

2.3.2.5.3 Separation Column. Type 316 Stainless steel 0.125 inch OD tubing x 18 feet long packed with Porapak Q 60/80 mesh; operated isothermally at 80° F.

2.3.3 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1.0 mm Hg in the 0 - 900 mm range.

2.3.4 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 inch Hg).

3. Reagents

3.1 Sampling.

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[1]Mention of trade names or specific products does not constitute endorsement by the EPA.

3.1.1 Filter. Glass fiber filter without organic binder, exhibiting at least 99.95 percent efficiency ($\leq$ 0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from suppliers quality control program are sufficient for this purpose.

3.1.2 Crushed Dry Ice.

3.2 Analysis.

3.2.1 (TGNMO) Analyzer.

3.2.1.1 Carrier Gas. 5 percent O_2 in N_2 containing less than 1 ppm organics.

3.2.1.2 Fuel Gas. 40 percent hydrogen in nitrogen containing less than 1 ppm organics.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. 5 percent O_2 in N_2 containing less than 1 ppm organics.

3.2.2.2 Oxygen. Oxygen containing less than 1 ppm organics.

3.3 Calibration.

3.3.1 (TGNMO) Analyzer.

3.3.1.1 Calibration Gases (3). Gas mixture standards with known propane (C_3H_8) concentrations corresponding to ranges of 5-10 ppm, 50-10 percent and 20-25 percent methane or carbon equivalent are prepared and certified by a gas manufacturer. The mixture shall consist of C_3H_8, CO, CO_2, and CH_4 in nitrogen. The gas manufacturer must recommend a maximum shelf life for each cylinder so that the C_3H_8 concentration does not change

more than ± 5 percent from its certified value. The date of gas cylinder preparation, certified C_3H_8, CO, CO_2, and CH_4 concentrations and recommended maximum shelf life must be affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards are to be used to prepare a chromatograph calibration curve as described in Section 4.4.1.1.

3.3.1.2 Span Gas. The calibration gas (Section 3.3.1.1) corresponding to 20 to 25 percent is used to span the analyzer.

3.3.1.3 Oxidation Catalyst Check. The calibration gas (Section 3.3.1.1) corresponding to 20 to 25 percent is used to check the oxidation catalyst.

3.3.1.4 Reduction Catalyst Check. A gas standard with a known concentration of 5 percent (nominal) CO_2 in nitrogen is used to check the reduction catalyst.

3.3.2 Condensate Recovery and Conditioning Apparatus. Gas mixture standards (2) with known propane (C_3H_8) concentrations in nitrogen corresponding to ranges of 5-10 ppm and 5-10 percent (methane or carbon equivalent) are prepared and certified by a gas manufacturer. These gas mixture standards are to be used to check the operation of the condensate trap oxidation system as described in Section 4.4.2.

4. Procedure

4.1 Sampling

4.1.1 Pretest Preparation. The sample tank shall be calibrated according to the procedure described in paragraph 4.4.3. Check filters visually against the light for irregularities,

flaws, or pinhole leaks. Either in the laboratory or in the field evacuate the sample tank to a vacuum of 755 mm mercury (measured by a mercury U-tube manometer). Record the temperature, barametric pressure, tank vacuum measured with the manometer, and the vacuum indicated on the tank gauge.

4.1.2 Assemble the system as shown in Figure 1. Immerse the condensate trap in dry ice and start the filter and probe heaters.

4.1.3 Leak check procedures.

4.1.3.1 Gas Sampling Tank Leak Check. Leak check the gas sampling tank immediately after the tank is evacuated. Once the tank is evacuated, allow the tank to sit for 30 minutes. The tank is acceptable if no change in tank vacuum (measured by the mercury manometer) is noted.

4.1.3.2 Pretest Leak Check. A pretest leak check is recommended, but not required. If the tester opts to conduct the pretest leak check, the following procedure is used. After the sampling train has been assembled (including cooling of condensate trap and heating of filter) plug the probe tip. Attach the vacuum line of the leak check apparatus (Figure 5) to the T-connector of the evacuated tank; open the valve on this connector (not the sample flow control valve to the evacuated tank) and evacuate the sample train to a vacuum of 625 mm Hg. Shut the valve on the pump side of the manometer and allow the sampling train to sit for 10 minutes. A leak rate in excess of 0.5 mm Hg for this 10 minute period is unacceptable. When the

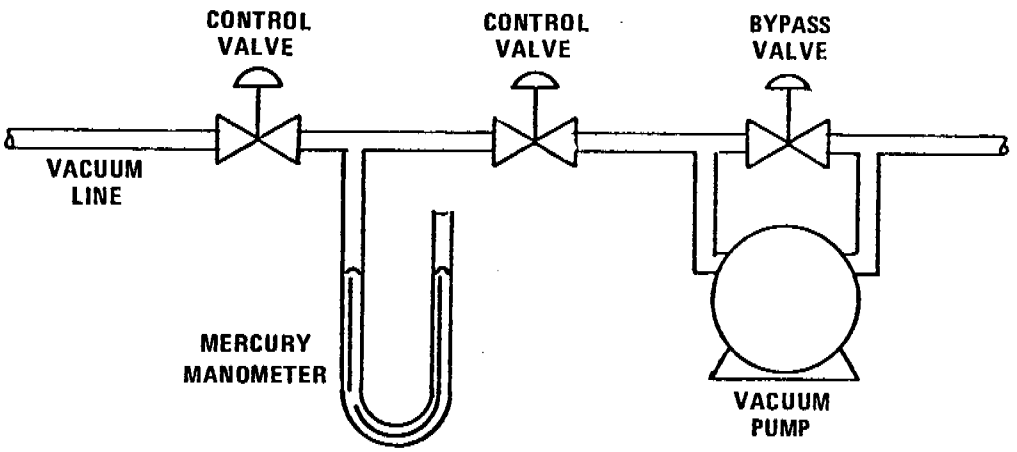


Figure 5. LEAK CHECK APPARATUS

leak check is completed, slowly release the vacuum in the train by unpluging the probe, close the T-connector valve, and plug this connector to assure a leak free system.

4.1.3.3 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, plug the end of the sampling probe and attach the vacuum line of the leak-check apparatus (Figure 5) to the evacuated tank t-connector. Assure that the flow valve to the evacuation pump (valve between manometer and pump) is closed. First open the t-connector valve to the manometer and then open the flow control valve to the evacuated tank. Record the clock time and tank vacuum. After 10 minutes note the tank vacuum. A leak rate in excess of 0.5 mm Hg for this ten minute period is unacceptable and the sampling run shall be voided. After completing the leak check, close the evacuated tank flow control valve and the t-connector flow control valve. Disconnect the leak check apparatus and plug the t-connector to assure a leakproof seal during shipping. Unplug the probe tip.

4.1.4 Sample Train Operation. Place the probe into the stack such that the probe tip is located at a pre-selected location. For stacks under negative pressure, assure that the sample port is sufficiently sealed to prevent leakage of ambient air around the probe. Record the clock time, sample tank gauge vacuum, and barometric pressure. Assure that the flow control needle valve is closed. Begin sampling by opening the evacuated tank flow valve all the way. Open the flow control needle valve until

the rotameter indicates the desired setting; maintain a constant flow rate (± 10 percent) throughout the duration of the sampling period. Record the gauge vacuum, rotameter setting, and filter temperature at 5 minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the standard; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained. When the sampling is completed, close the evacuated tank valve and remove the probe from the stack. Record the final readings. Conduct the post test leak check according to the procedures of paragraph 4.1.3.3.

If the sampling must be stopped before obtaining the minimum sampling time specified in the applicable subpart because a constant flow rate cannot be maintained, proceed as follows: After removing the probe from the stack, conduct the post test leak check. After the leak check is completed, remove the evacuated tank from the sampling train (without disconnecting other portions of the sampling train) and connect another evacuated tank to the sampling train. Proceed with the sampling; after the minimum total sampling time is exceeded, end the test.

4.2 Sample Recovery.

Disconnect the condensate trap at the filter and at the flow metering system. Tightly seal the ends of the condensate trap; keep the trap packed in dry ice until analysis is conducted. Seal the connection at the evacuated tank to assure a leak proof seal during shipping. After the evacuated tank has cooled to ambient

conditions, attach the U-tube manometer to the t-connector, open the valve, and record the tank vacuum, ambient temperature, barometric pressure, and indicated gauge vacuum. Close the flow valve and reseal the t-connector to assure a leak proof seal during shipping. Assure that the test run number is properly indentified on the condensate trap and evacuated tank(s).

4.3 Analysis

4.3.1 TGNMO Analyzer. Heat the catalysts to their operating temperatures and set the carrier gas and fuel flow rates. Conduct the calibration check required in paragraph 4.4.1.1 and the catalyst performance checks required in paragraph 4.4.1.2 prior to analyzing the test samples.

4.3.2 Condensate Trap. Return the condensate trap to the laboratory and hook it into the recovery and conditioning system (Figure 3). Set the oven for the oxidizing catalyst at 850° C and the trap heating furnace at 600° C. Set the gas directing valve to permit flow of 5 percent O_2/N_2 through channel A to the condensate trap at a rate of 80 cc/min; at the same time set the oxygen flow through channel B at 20 cc/min (1:4 ratio). After two minutes, switch the gas directing valve to permit the oxygen to flow via channel A directly through the condensate trap and the 5 percent O_2/N_2 carrier gas to flow through channel B. When the NDIR indicates that CO_2 is no longer being emitted from the combustion system, shut off the collection flask from the system and cease combustion. Record the collection flask pressure after combustion is completed (P_i) and then pressurize the flask to 860 mm Hg (nominal) with nitrogen and record the final pressure

(P_f). Remove a syringe sample from the flask and inject this into the TGNMO analyzer. Record the analyzer response (ppm C) for triplicate samples.

4.3.3 Gas Sampling Tank. Using a U-tube mercury manometer, record the tank vacuum (P_t). Pressurize the tank with nitrogen and record the final tank pressure (P_{t_f}), temperature and barometric pressure. Remove a syringe sample from the tank and inject this into the TGNMO analyzer. Record the analyzer response (ppm C) for the non-methane organic fraction for triplicate samples.

4.4 Calibration. Maintain a record of performance of each item.

4.4.1 TGNMO Analyzer.

4.4.1.1 Calibration Curve. Determine the linearity of the analyzer for TGNMO as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respective zeroing controls to indicate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these two steps until adjustments are no longer necessary. Calculate a predicted response for the 5-10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If this value is not within $\pm$ 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any

event, this linearity performance specification shall be met before the analyzer is placed in actual use.

4.4.1.2 Catalyst Performance Check. These checks should be performed on a frequency established by the amount of use of the analyzer and the nature of the organic emissions to which it is exposed. To confirm that the oxidation catalyst is functioning in the correct manner, the operator must turn off or bypass the reduction catalyst while operating the analyzer in an otherwise normal fashion. Inject the calibration gas (paragraph 3.3.1.3) into the system. If oxidation is adequate, the only gas that will then reach the detector will be CO_2, to which the FID has no response. If a response is noted, the oxidation catalyst must be replaced. To confirm the proper operation of the reduction catalyst, inject a sample of the CO_2 calibration gas (Section 3.3.1.4) into the system. If the CO_2 is not reduced to CH_4 as it should be, then the reduction catalyst must be replaced or regenerated.

4.4.2 Condensate Trap Oxidation Catalyst. Inject syringe samples of the calibration gases listed in Section 3.3.2 into the sample port of the condensate trap combustion system (Figure 3). Proceed with a normal analysis (i.e., collection of the CO_2 in the flask followed by analysis of triplicate aliquots using the TGNMO analyzer) and compare results to the actual concentration. Repair the system if the results (average of triplicate aliquots) deviate by greater than $\pm$ 5 percent from the calibration gas value.

4.4.3 Gas Sampling Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in

service, determine the tank volume by weighing the tanks empty and then filled with water; weigh to the nearest 0.5 gm and record the results.

4.4.4 Intermediate Collection Flask. The volume of the intermediate collection flasks used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each flask in service, determine the volume by weighing the flasks empty and then filled with water; weigh to the nearest 0.5 gm and record the results.

4.4.5 Condensate Trap Leak Check. Prior to each use, check each condensate trap for leaks by pressurizing with N_2 to approximately 50 psig and immersing in water.

4.4.6 Rotameter. The rotameter need not be calibrated but should be cleaned and maintained according to the manufacturer's instruction.

5. Calculations

5.1 Sample Volume. For each test run calculate the gas volume sampled:

$$V_s = 0.36\ V\left(\frac{P_t}{T_t} - \frac{P_{t_i}}{T_{t_i}}\right)$$

5.2 Noncondensible TGNMO. For each collection tank, determine the concentration of TGNMO (ppm C):

$$C = 3 \times \frac{P_{t_f}}{P_t} \times \frac{T_t}{T_{t_f}} \times \sum_{j=1}^{m} C_{p_j}$$

5.3 Condensible TGNMO. For each condensate trap determine the concentration of TGNMO (ppm C):

$$C_c = \frac{3 \times V_f \times P_f}{V_s \times P_i} \times \sum_{k=1}^{n} C_{cp_k}$$

5.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C_t = C + C_c$$

5.5 Control Device Efficiency. To determine the TGNMO control device efficiency for each test run, use the following equation:

$$E = \frac{C_{ti} - C_{to}}{C_{ti}} \times 100$$

where:

C = Noncondensible TGNMO calculated concentration, ppm carbon equivalent.

C_p = TGNMO analyzer measured concentration for gas collection tank, ppm propane.

C_c = Condensible TGNMO (condensate trap) calculated concentration, ppm carbon equivalent.

C_{cp} = TGNMO analyzer measured concentration for intermediate collection flask, ppm propane.

C_t = Total gaseous nonmethane organic (TGNMO), ppm carbon equivalent.

C_{to} = TGNMO at control device outlet, ppm carbon equivalent.

C_{ti} = TGNMO at control device inlet, ppm carbon equivalent.

E = Control device efficiency, percent.

P_f = Final pressure of intermediate collection flask (nominal 860 mm Hg.), mm Hg, absolute.

P_i = Pressure of intermediate collection flask at completion of combustion, mm Hg, absolute.

P_{t_i} = Gas sample tank pressure prior to sampling, mm Hg, absolute.

P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg, absolute.

P_{t_f} = Final gas sample tank pressure after pressurizing, mm Hg, absolute.

T_{t_i} = Gas sample tank temperature prior to sampling, °K.

T_t = Gas sample tank temperature at completion of sampling, °K.

T_{t_f} = Gas sample tank temperature after pressurizing, °K.

V = Gas collection tank volume, M^3

V_f = Intermediate collection tank volume, M^3

V_s = Gas volume sampled, dscm

m = Total number of injections of non-condensible TGNMO during analysis (where j = injection number, 1 . . . m)

n = Total number of injections of condensible TGNMO during analysis (where k = injection number, 1 . . . n)

0.36 = 273°K/760 mm Hg

Standard Conditions = Dry, 760 mm Hg, 273°K.

6. Bibliography

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ATTACHMENT 3. ALTERNATE TEST METHOD FOR DIRECT MEASUREMENT OF TOTAL GASEOUS ORGANIC COMPOUNDS USING A FLAME IONIZATION ANALYZER

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the performance characteristics of the flame ionization detector, nor by those who are unfamiliar with source sampling.

1. Principle and Applicability

1.1 Principle. The sample is drawn from the source, through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Ions formed in the combustion of a specific hydrocarbon compound in a H_2 - O_2 flame establish a current that is proportional to the mass flow rate of that hydrocarbon to the flame. This current is collected at two polarized electrodes, and is read out on a potentiometric recorder and compared with a calibration curve based on propane (C_3H_8), or an organic solvent, as appropriate. The results are reported as equivalents of methane (CH_4) or carbon, or in terms of an organic solvent.

1.2 Applicability. This method is applicable for the determination of the true carbon mass concentration, and/or an indicated volume or mass concentration (expressed in terms of carbon or of an assumed organic compound, e.g., methane equivalent) of gaseous organic compounds present in an emission stream. It can also be used to measure the mass concentration of an organic solvent if stable mass standards of the solvent can be generated.

The measurement will not exclude methane, so a supplemental measurement of methane may be necessary.

2. Range and Sensitivity

2.1 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

3.1 Nonorganic Gases. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor. however, the analyzer response to organics will be affected by the composition of the background or carrier gas. It is, therefore, required that the calibration gases be contained in air, which is most likely to be the same carrier gas as that of the actual sample.

Investigation of a reported oxygen synergism[2] has shown that a 40/60 mixed fuel (40 percent H_2, 60 percent He) is required if the oxygen content of the emission stream varies more than a few percent from its mean value. Mixed fuel will also be required if the oxygen content of the emission stream varies more than a few percent from the oxygen content of the calibration gases.

3.2 Organic compounds. Acetylenic compounds give a slightly higher response than aliphatic compounds. Carbon atoms bound to oxygen, nitrogen, or halogens give a reduced or zero response.

Table 1[3] illustrates these effects in terms of the relative response of one FIA to various hydrocarbons. The response is shown as effective carbon number (ECN), as follows:

$$ECN = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$

These values are true for one mode of operation of a specific detector under specific conditions (e.g., mixed N_2, H_2 fuel). It has been reported that these numbers may vary widely for different operating conditions and for different detectors. Variations of as much as 25 percent have been observed in studies of the types of organics associated with automotive emissions. The variation was observed to decrease with decreasing sample flow rate, but with an accompanying decrease in sensitivity.[7]

TABLE 1. APPROXIMATE EFFECTIVE CARBON NUMBERS (FROM BECKMAN INSTRUMENTS)

Type of Atom	Occurrence	Effective Carbon Number
Carbon	In Aliphatic Compound	+1.0
Carbon	In Aromatic Compound	+1.0
Carbon	In Olefinic Compound	+0.95
Carbon	In Acetylenic Compound	+1.30
Carbon	In Carbonyl Radical	0.0
Carbon	In Nitrite	+0.3
Oxygen	In Ether	-1.0

TABLE 1. APPROXIMATE EFFECTIVE CARBON NUMBERS
(FROM BECKMAN INSTRUMENTS)
(Continued)

Type of Atom	Occurrence	Effective Carbon Number
Oxygen	In Primary Alcohol	-0.6
Oxygen	In Secondary Alcohol	-0.75
Oxygen	In Tertiary Alcohol, Ester	-0.25
Chlorine	As two or more chlorine atoms on single aliphatic carbon atom	-0.12 each
Chlorine	In Olefinic Carbon Atom	+0.05
Nitrogen	In Amine	Value similar to that for oxygen atom in corresponding alcohol

From this information it can be seen that the accuracy of this method for a given source will be largely dependent on the particular makeup of organic emissions from the source.

3.3 Other effects. Significant changes in viscosity of the emission gas from that of the calibration gas will affect the mass rate of organics to the detector. If this phenomena is expected to occur, a corrective technique must be devised.

If the instrument is calibrated with organic solvent standards, and then used to measure emissions of that solvent, their response variations have been calibrated out.

4. Apparatus

4.1 Commercially available heated FIA. The analyzer should

7.2.2.1 Solvent Standards Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

All measurements or calculations must be corrected for CH_4, if required by the emission regulation.

8.1 Carbon or Surrogate Organic Compound Concentration.

8.1.1 Volume concentration [ppm]. To determine emission concentrations of total gaseous organics (wet basis) on a CH_4 or carbon equivalent basis, multiply the recorded emission values by the number of carbon atoms in a molecule of calibration gas. In some instances it will be required to report emissions on the basis of the calibration gas, in which case no calculations are necessary.

8.1.2 Mass concentration [mg/m^3]. To convert volume concentration to mass concentration, proceed as follows:

8.1.2.1 Establish Standard Conditions. Find the volume occupied by 1 mg. mole of ideal gas at these conditions. Then find the number of mg. moles in 1 m^3 (at saturation).

8.1.2.2 Determine the molecular weight of the assumed organic compound in which the emission is to be expressed.

8.1.2.3 Use the values obtained in 8.1.2.1 and 8.1.2.2 to determine the mass concentration (mg/m^3) at saturation. Divide this number by 10^6 to find the mg/m^3 equivalent to 1 ppm.

8.1.2.4 Multiply the result obtained in 8.1.2.3 by the volume concentration obtained in 8.1.1. The result is the mass concentration expressed in terms of the compound whose molecular weight was determined in 8.1.2.2.

8.2 Organic Solvent Concentration

8.2.1 Solvent Standards Concentrations. Calculate each solvent standard concentration prepared in accordance with Section 7.2.1.2 as follows:

$$C_c = \frac{B(d.\ \frac{mg}{\mu l})\ \frac{10^3\ \mu g}{mg}}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 1}$$

where:

C_c = Solvent standard concentration, µg/l.

B = Number of µl of solvent injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter, calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

d. = Density of the solvent at 293°A.

8.2.2 Solvent Emission Concentrations The emission values in μg/ml are taken from the solvent standards response curve. No further calculations are required.

9. References

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document discusses the rationale of total volatile organics stationary source emission measurement through the determination of organic carbon mass concentration. A conceptual approach for writing emission regulations in terms of volatile organic carbon is recommended, and drafts of two specific test methods are presented for regulation implementation. The methods are the measurement of total gaseous nonmethane organics as carbon by the chromatographic oxidation/reduction procedure, and the relative organic measurement derived by direct application of the flame ionization analyzer.

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A Guideline for Surface Coating Calculations

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A Guide For Surface Coating Calculations

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ABSTRACT

The calculation of volatile organic compound emissions from surface coating operations to determine compliance is often a complicated task, sometimes causing confusion with compliance authorities and sources alike. In an attempt to minimize this confusion, EPA (OAQPS) has periodically issued guidance in this area, generally in the form of memoranda to the EPA Regional Offices. Guidance for submitting data on surface coatings and performing basic calculations is contained in the document entitled "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings," EPA 450/3-84-019, published in December 1984.

"A Guideline for Surface Coating Calculations" takes the above guidance one step further. Example calculations are included for basic emission problems, compliance determinations, equivalency determinations, application of transfer efficiency, and calculations involving complex multiproduct coatings. Graphs and tables useful in approximating and double-checking these calculations are also included.

SECTION 1

INTRODUCTION

1.1 BACKGROUND

Surface coating entails the deposition of a solid film on a surface through the application of a coating material such as paint, lacquer, or varnish. Surface coating operations are significant volatile organic compound (VOC) emission sources. Most coatings contain VOCs which evaporate during the coating application and curing processes, rather than becoming part of the dry film.

The U.S. Environmental Protection Agency (EPA) has issued Control Techniques Guidelines (CTGs) for many surface coating operations, including cans, metal coils, paper, fabric, automobiles, light-duty trucks, metal furniture, large appliances, magnet wire, miscellaneous metal parts and products, graphic arts, and flatwood paneling. The emission limits recommended in these guidelines have been adopted by many state and local agencies. The EPA has also issued new source performance standards (NSPS) for many surface coating operations, including automobile, light-duty trucks, beverage cans, metal coils, large appliances, metal furniture, pressure sensitive tapes and labels, vinyl printing and topcoating, and publication rotogravure printing.

To comply with these regulations, a surface coating operator might elect to change to low VOC content coatings, to use add-on controls such as incineration or carbon adsorption, or to improve transfer efficiency. In cases where compliance is achieved by a change in coating alone, VOC emissions can be calculated from the VOC content of the coating as applied to the substrate. When add-on controls or transfer efficiency improvements are used, more complex calculations can be performed to determine the effectiveness of the control strategy. It is more convenient (and frequently more reliable) to establish VOC compliance or non-compliance through these calculations than it is to measure total VOC emissions directly.

The emission limits for existing sources recommended in the CTGs and adopted by many state and local agencies are expressed in terms of pounds of VOC per gallon of coating less water. These units are directly useful only for cases where compliance is achieved with low VOC content coatings alone. When add-on controls or transfer efficiency improvements are used, compliance calculations must be done on an equivalent solids basis. The reasons for this are explained graphically in Glossary of Air Pollution Control of Industrial Coating Operations, EPA-450/3-83-013R, December 1983. Pages 26-29 of this document are located in Appendix A. The emission limits in most surface coating NSPSs are expressed in terms of pounds of VOC per gallon of coating solids applied. The reader should review this concept in Appendix A before continuing in this guideline manual. This calculation guide assumes that the solids used or applied in a specific process remain constant for a given example (solids equivalency).

1.2 DESCRIPTION OF VOC CALCULATIONS

This document presents sample calculations typical of those used to determine compliance or to evaluate control strategies. These step-by-step calculations are accompanied by explanations that are useful to persons unfamiliar with surface coating operations. Basic calculations are included along with calculations to determine compliance and equivalency (necessary for evaluating bubbles, offsets, netting, etc.). Transfer efficiency problems requiring a series of calculations are included.

The basis for most of the sample calculations is the information and procedures discussed in Procedure for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings, EPA-450/3-84-019, December 1984, which is reprinted as Appendix B of this report and referred to as the "VOC Data Sheets". The first VOC Data Sheet provides information on the VOCs present in a coating when it is sold by the manufacturer to the coater. This is referred to as the VOC content of the coating "as supplied by the coating manufacturer to the user." The second VOC Data Sheet provides information on the VOCs present in the coating as it is used by the coater and includes the effect of dilution solvent added before application. This is referred to as the VOC content "as applied to the substrate by the user." For

dip or flow coating operations, this should include any make-up solvent which is added to a coating to replace evaporated solvent and therefore maintain a specific viscosity of the coating being applied. The calculations in this document assume that the inspector has obtained the coating data from the VOC Data Sheets. However, it is up to the inspector to verify this data. EPA Reference Method 24 or individual ASTM methods are the final judge in determining compliance. Appendix C contains a copy of Reference Method 24.

Some confusion may exist regarding the meanings and proper uses of terms. As defined in Appendix B, the term "as applied" means the condition of a coating after dilution by the user just prior to application to the substrate. However, the term "solids applied" means the amount coating solids that actually adheres to the object being coated, not the amount of solids leaving the applicator. In contrast, the term "solids used" refers to the total amount of solids used in an application, not the amount of solids that actually adheres to substrate. Care should be taken when using these terms to avoid confusion.

1.3 NEGLIGIBLY PHOTOCHEMICALLY REACTIVE MATERIALS

A volatile organic compound is defined in 40 CFR Subpart A, General Provisions, §60.2, as any organic compound which participates in atmospheric photochemical reactions; or which is measured by a reference method, an equivalent method, or an alternative method; or which is determined by procedures specified under any subpart. The EPA considers the following organic solvents to have negligible photochemical reactivity, and therefore does not consider them to be VOCs:

Methane[1]
Ethane[1]
1,1,1-trichloroethane (methyl chloroform)[1]
Methylene chloride[2]
Trichlorofluoromethane (CFC-11)[3]
Dichlorodifluoromethane (CFC-12)[3]
Chlorodifluoromethane (CFC-22)[3]
Trifluoromethane (CFC-23)[3]
Trichlorotrifluoroethane (CFC-113)[1]

Dichlorotetrafluoroethane (CFC-114)[3]

Chloropentafluoroethane (CFC-115)[3]

Many states also do not consider some or all of these materials to be VOCs.

Two of these compounds, 1,1,1-trichloroethane and methylene chloride, are used as solvents in some coatings. These materials should not be counted as VOCs if they are "exempt" from the applicable regulation. The method for discounting these materials is described in some of the examples and in Appendix B. Generally, these materials, when "exempt" from the applicable regulation, are treated in the same manner as water in emission calculations.

Only the compounds listed above and any compounds given the status of "negligibly photochemically reactive" by the U.S. EPA in a future Federal Register may be considered as exempt from Federal enforcement of applicable State SIP VOC regulations. Also, Rule 66 should not be referenced for exempting compounds as per 42 FR 35314, July 8, 1977.

[1]42 FR 35314, July 8, 1977

[2]45 FR 32042, June 4, 1979

[3]45 FR 48941, July 22, 1980

SECTION 2

BASIC CALCULATIONS

This section presents examples of basic types of calculations. The examples closely follow the VOC Data Sheets (Appendix B).

2.1 DETERMINING THE MASS OF VOC EMITTED PER VOLUME OF SOLIDS

Example 1 -

Determine the mass of VOC emitted per volume of solids for a solvent-borne coating. The following data are given:

A.	Coating Density	= 10.0 lb/gal
B.	Total Volatiles	= 60 percent by weight
C.	Water Content	= 0
D.	Organic* Volatiles Content	= 60 percent by weight
E.	Nonvolatiles Content (Solids)	= 35 percent by volume

Mass of VOC emitted per volume of solids is:

$$\frac{10.0 \text{ lb coating}}{\text{gal coating}} \times \frac{0.60 \text{ lb VOC}}{\text{lb coating}} \times \frac{1 \text{ gal coating}}{0.35 \text{ gal solids}} = \frac{17.1 \text{ lb VOC}}{\text{gal solids}}$$

- -

Example 2 -

Determine the mass of VOC emitted per volume of solids for a waterborne coating. The following data are given:

A.	Coating Density	= 9.0 lb/gal
B.	Total Volatiles	= 70 percent by weight
C.	Water Content	= 30 percent by weight
D.	Organic* Volatiles Content	= 70-30=40 percent by weight
E.	Nonvolatiles Content (Solids)	= 19.6 percent by volume

*Photochemically reactive materials only.

Mass of VOC emitted per volume of solids is:

$$\frac{9.0 \text{ lb coating}}{\text{gal coating}} \times \frac{0.40 \text{ lb VOC}}{\text{lb coating}} \times \frac{1 \text{ gal coating}}{0.196 \text{ gal solids}} = \frac{18.4 \text{ lb VOC}}{\text{gal solids}}$$

Example 3 -

Determine the mass of VOC emitted per volume of solids for a coating that contains some negligibly photochemically reactive (NPR) solvents. The following data are given:

A.	Coating Density	= 11.0 lb/gal
B.	Total Volatiles	= 80 percent by weight
C.	NPR Solvent Content	= 40 percent by weight
D.	Organic* Volatiles Content	= 40 percent by weight
E.	Nonvolatiles Content (Solids)	= 15 percent by volume

Mass of VOC emitted per volume of solids is:

$$\frac{11.0 \text{ lb coating}}{\text{gal coating}} \times \frac{0.40 \text{ lb VOC}}{\text{lb coating}} \times \frac{1 \text{ gal coating}}{0.15 \text{ gal solids}} = \frac{29.3 \text{ lb VOC}}{\text{gal solids}}$$

2.2 DETERMINING THE MASS OF VOC EMITTED PER VOLUME OF COATING LESS WATER

Example 4 -

Determine the mass of VOC emitted per volume of coating less water for a solvent-borne coating. The following data are given:

A.	Coating Density	= 10 lb/gal
B.	Total Volatiles	= 60 percent weight
C.	Water Content	= 0
D.	Organic* Volatiles Content	= 60 percent weight

Mass of VOC per volume of coating less water is:

$$\frac{10 \text{ lb coating}}{\text{gal coating}} \times \frac{0.60 \text{ lb VOC}}{\text{lb coating}} \times \frac{1 \text{ gal coating}}{(1-0) \text{ gal coating less water}}$$

$$= \frac{6 \text{ lb VOC}}{\text{gal coating less water}}$$

*Photochemically reactive materials only.

Example 5 -

Determine the mass of VOC emitted per volume of coating less water for a water-borne coating. The following data are given:

A. Coating Density	= 9.0 lb/gal
B. Total Volatiles	= 70 percent by weight
C. Water Content	= 30 percent by weight
D. Organic* Volatiles Content	= 70-30=40 percent by weight

The mass of water in the coating is:

$$\frac{9.0 \text{ lb coating}}{\text{gal coating}} \times \frac{0.3 \text{ lb water}}{\text{lb coating}} = \frac{2.7 \text{ lb water}}{\text{gal coating}}$$

The volume of water in the coating is:

$$\frac{2.7 \text{ lb water}}{\text{gal coating}} \times \frac{1}{\frac{8.33 \text{ lb water}}{\text{gal water}}} = \frac{0.32 \text{ gal water}}{\text{gal coating}}$$

The mass of VOC in the coating is:

$$\frac{9.0 \text{ lb coating}}{\text{gal coating}} \times \frac{0.4 \text{ lb VOC}}{\text{lb coating}} = \frac{3.6 \text{ lb VOC}}{\text{gal coating}}$$

The mass of VOC emitted per volume of coating less water is:

$$\frac{\frac{3.6 \text{ lb VOC}}{\text{gal coating}}}{\frac{1 \text{ gal coating} - 0.32 \text{ gal water}}{\text{gal coating}}} = \frac{5.3 \text{ lb VOC}}{\text{gal coating less water}}$$

- -

Example 6 -

Determine the mass of VOC emitted per gallon of coating less negligibly photochemically reactive material for a coating that contains some negligibly photochemically reactive material.

The following data are given:

A. Coating Density	= 10.5 lb/gallon
B. Total Volatiles	= 80 percent by weight
C. NPR Solvent Content	= 40 percent by weight
D. Organic* Volatiles Content	= 40 percent by weight
E. NPR Solvent Density	= 11.0 lb/gal

*Photochemically reactive materials only.

The mass of VOC per volume of coating is:

$$\frac{10.5 \text{ lb coating}}{\text{gal coating}} \times \frac{0.4 \text{ lb VOC}}{\text{lb coating}} = \frac{4.2 \text{ lb VOC}}{\text{gal coating}}$$

The mass of NPR solvent in the coating is:

$$\frac{10.5 \text{ lb coating}}{\text{gal coating}} \times \frac{0.4 \text{ lb NPR solvent}}{\text{lb coating}} = \frac{4.2 \text{ lb NPR solvent}}{\text{gal coating}}$$

The volume of NPR solvent in the coating is:

$$\frac{4.2 \text{ lb NPR solvent}}{\text{gal coating}} \times \frac{1}{\frac{11.0 \text{ lb NPR solvent}}{\text{gal NPR solvent}}} = \frac{0.38 \text{ gal NPR solvent}}{\text{gal coating}}$$

The mass of VOC per gallon of coating less NPR solvent is:

$$\frac{\frac{4.2 \text{ lb VOC}}{\text{gal coating}}}{\frac{1 \text{ gal coating} - 0.38 \text{ gal NPR solvent}}{1 \text{ gal coating}}} = \frac{6.8 \text{ lb VOC}}{\text{gal coating less NPR solvent}}$$

SECTION 3
TRANSFER EFFICIENCY

When spray guns are used to apply coatings, much of the coating material either bounces off the surface being coated or misses it altogether. Transfer efficiency (TE) is the ratio of the amount of coating solids deposited on the coated part to the amount of coating solids used. Regardless of the TE, all of the VOCs in the dispensed coating are emitted whether or not the coating actually reaches and adheres to the surface. Consequently, improved TE can reduce VOC emissions because less coating is used. EPA has defined baseline transfer efficiencies of 60 percent for RACT in metal furniture and appliance coating and 30 percent for RACT waterborne equivalence in the automobile industry (for both primer-surfacer and topcoat applications). If a base TE has not been documented by EPA, then the company must satisfactorily document their base TE prior to equivalency calculations/demonstrations. To obtain TE credits, a company must prove its baseline TE with documentation, and document the new TE.

3.1 DETERMINING THE MASS OF VOC EMITTED PER VOLUME OF SOLIDS APPLIED

Example 1 -

Determine the mass of VOC emitted per volume of solids applied given the following data:

A. VOC content of coating = $\frac{4.0 \text{ lb VOC}}{\text{gal solids}}$

B. Transfer efficiency = 40 percent

Mass of VOC emitted per volume of solids applied is:

$$\frac{4.0 \text{ lb VOC}}{\text{gal solids}} \times \frac{1 \text{ gal solids used}}{0.4 \text{ gal solids applied}} = \frac{10.0 \text{ lb VOC}}{\text{gal solids applied}}$$

- -

Example 2 -

Determine the mass of VOC emitted per volume of solids applied given the following data:

A. VOC content of coating = 3.0 lb VOC/gal coating less water
B. Nonvolatiles content = 55 percent by volume
C. Transfer efficiency = 60 percent
D. Water Content = None

$$\frac{3.0 \text{ lb VOC}}{\text{gal coating less water}} \times \frac{1 \text{ gal coating less water}}{0.55 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.60 \text{ gal solids applied}}$$

$$= \frac{9.1 \text{ lb VOC}}{1 \text{ gallon solids applied}}$$

Note: For a waterborne coating, be careful of using pounds of VOC per gallon of coating less water and volume nonvolatiles content as a fraction of the total coating including water. These two items cannot simply be combined to get pounds of VOC per gallon of solids. The best method is to follow Example 2 in Section 2 and then factor in transfer efficiency. Alternatively, the volume nonvolatiles content could be determined for the coating less water if the volume fraction water is known or calculated as follows:

$$\text{Volume fraction nonvolatiles in coating less water} = \frac{\text{volume fraction nonvolatiles in coating including water}}{1 - \text{volume fraction water}}$$

- -

3.2 CALCULATING AVERAGE TRANSFER EFFICIENCY

Example 3 -

A plant operates two coating lines. Each line uses both manual electrostatic spray guns (TE = 60 percent) and rotating-head electrostatic spray guns (TE = 80 percent). Table 1 contains the applicable data. What is the average transfer efficiency?

$$\text{Average TE} = \frac{\text{total liters of solids deposited}}{\text{total liters of solids used}} = \frac{38.4 + 36.8}{64 + 46} \times 100$$

$$= \frac{75.2}{110} \times 100 = 68 \text{ percent}$$

TABLE 1. EXAMPLE CALCULATION OF AVERAGE TE WHEN SEVERAL DIFFERENT COATING APPLICATION METHODS ARE USED

Coating line	Total liters of coating used	Volume percent solids	Total liters of solids used	Application Method: Manual electrostatic spray (TE = 60%)* Liters of coating used	Manual electrostatic spray (TE = 60%)* Liters of solids used	Manual electrostatic spray (TE = 60%)* Liters of solids deposited	Rotating-head electrostatic spray (TE = 80%)* Liters of coating used	Rotating-head electrostatic spray (TE = 80%)* Liters of solids used	Rotating-head electrostatic spray (TE = 80%)* Liters of solids deposited
A	100	50	50	80	40	24	20	10	8
B	100	60	60	40	24	14.4	60	36	28.8
TOTAL					64	38.4		46	36.8

*These TE values are illustrative values only. Actual TE must be determined to calculate actual emissions.

SECTION 4

COMPLIANCE DETERMINATIONS

4.1 CALCULATING COATING COMPLIANCE WITH A STANDARD

Example 1 -

A coater is required to meet an emission limit of 3.5 pounds of VOC per gallon of coating less water. Does a coating with a density of 12 pounds per gallon that contains 25 weight percent VOC comply? The coating contains no water or negligibly photochemically reactive solvents.

$$\frac{12 \text{ lb coating}}{\text{gal coating}} \times \frac{0.25 \text{ lb VOC}}{\text{lb coating}} \times \frac{1 \text{ gal coating}}{(1-0) \text{ gal coating less water}}$$

$$= \frac{3 \text{ lb VOC}}{\text{gal coating less water}}$$

So, the coating complies with the regulation.

- -

Example 2 -

A coater is required to meet an emission limit of 4.0 pounds VOC per gallon of solids. Does a coating with a density of 10 pounds per gallon that contains 60 weight percent volatiles, 45 weight percent water, and 30 volume percent solids comply?

The weight percent organic volatiles is 60-45=15.

The VOC content of the coating is:

$$\frac{10 \text{ lb coating}}{\text{gal coating}} \times \frac{0.15 \text{ lb VOC}}{\text{lb coating}} \times \frac{1 \text{ gal coating}}{0.30 \text{ gal solids}} = \frac{5 \text{ lb VOC}}{\text{gal solids}}$$

So, the coating does not comply with the regulation.

- -

Example 3 -

A coater is required to meet an emission limit of 10 pounds VOC per gallon of solids applied. Does the coating in Example 2 comply if it is applied at a transfer efficiency of 80 percent?

$$\frac{5 \text{ lb VOC}}{\text{gal solids}} \times \frac{1 \text{ gal solids used}}{0.80 \text{ gallon solids applied}} = \frac{6.3 \text{ lb VOC}}{\text{gal solids applied}}$$

So, the coating meets the regulation.

- -

Example 4 -

A metal furniture coater uses a coating containing 0.40 kg VOC/liter of coating (less water and exempt solvents). The coating contains 55 volume percent solids. The transfer efficiency is 87 percent. Is the plant in compliance if the maximum allowable emissions are 1.0 kg VOC/liter solids applied?

The solution is found by using the following basic equation:

$$\frac{\text{mass of VOC used}}{\text{volume of coating solids used}} \times \frac{1}{TE} = \frac{\text{mass of VOC used}}{\text{volume of coating solids applied}}$$

Emissions are:

$$\frac{0.40 \text{ kg VOC}}{1 \text{ liter of coating less water and exempt solvents}} \times \frac{1 \text{ liter of coating less water and exempt solvents}}{0.55 \text{ liter solids}} \times$$

$$\frac{1 \text{ liter solids}}{0.87 \text{ liter solids applied}} = \frac{0.84 \text{ kg VOC}}{1 \text{ liter solids applied}}$$

Since 0.84 is less than 1.0, the coating operation is in compliance.

Note: This example is similar to Example 2 in Section 3.1. Therefore, the note mentioned after Example 2 applies to this example too.

- -

4.2 CALCULATING COMPLIANCE WHEN ADD-ON CONTROLS ARE USED

Example 5 -

A coater is required to meet an emission limit of 6 pounds of VOC per gallon of solids. What percent emission reduction is needed if the coater uses a coating with 22 pounds of VOC per gallon of solids?

$$\frac{22-6}{22} \times 100 = \frac{16}{22} \times 100 = 73 \text{ percent emission reduction}$$

- -

Example 6 -

A coater is required to meet an emission limit of 3.7 pounds of VOC per gallon of coating less water. What percent emission reduction is needed if the coater uses a solvent-borne coating with 5.0 pounds of VOC per gallon of coating less water and a volume solids content of 25 percent?

This calculation must be done on a solids basis. First, the emission limit must be converted to pounds of VOC per gallon of solids. To do this, an assumed VOC density of 7.36 pounds per gallon is used to calculate the volume solids content of the "presumptive" RACT coating.

$$\frac{3.7 \text{ lb VOC}}{\text{gal coating less water}} \times \frac{1 \text{ gal VOC}}{7.36 \text{ lb VOC}} \times 100 = 50 \text{ volume percent VOC}$$

$$100-50 = 50 \text{ volume percent solids}$$

$$\frac{3.7 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.50 \text{ gal solids}} = \frac{7.4 \text{ lb VOC}}{\text{gal solids}}$$

Next, the VOC content of the coating used must also be calculated on a solids basis.

$$\frac{5.0 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.25 \text{ gal solids}} = \frac{20 \text{ lb VOC}}{\text{gal solids}}$$

Now the required percent reduction can be calculated.

$$\frac{20-7.4}{20} \times 100 = 63 \text{ percent emission reduction}$$

Notes:

1. An erroneous result is obtained if this calculation is not done on a solids basis. Using pounds of VOC per gallon of coating less water the result would be:

$$\frac{5.0-3.7}{5.0} \times 100 = 26 \text{ percent emission reduction}$$

This would not give equivalent emissions as it does not take into account that the "presumptive" RACT coating not only has lower VOC content, but higher solids content as well.

2. An assumed VOC density of 7.36 pounds per gallon is used to calculate the volume solids content of the "presumptive" RACT coating because this same value was used to determine the "presumptive" recommended RACT emission limits from volume solids data.

3. The volume solids content of actual coatings should be determined directly from coating formulation data as described in the VOC Data Sheets. Ocassionally, it may be useful to back calculate volume solids from VOC content and actual solvent or VOC density, but this must be done with extreme caution. When an inspector gathers data on the actual coatings used at a facility, the volume solids content should be obtained from coating formulation data from the facility or the coating manufacturer. The volume solids content should not be back calculated.

SECTION 5

EQUIVALENCY DETERMINATIONS

Equivalency calculations are required when compliance decisions must be made for replacement coatings, bubbles, offsets, netting, etc. This type of calculation relates primarily to the CTG source categories. This section presents example equivalency calculations.

VOC equivalency calculations must be made on a solids basis. The amount of solids needed to coat a surface to a particular film thickness is the same regardless of the coating composition used. Reducing the solids content of an organic solvent-borne coating increases the quantity of coating required and increases VOC emissions because more coating is used and the coating has a higher VOC content.

5.1 CALCULATING ALLOWABLE HOURLY EMISSIONS FOR A SOLVENT-BORNE COATING*

Example 1 -

A surface coater uses 10 gallons per hour of a coating that contains 5.5 lb VOC per gallon of coating and 25 volume percent solids. New regulations indicate that the coating formulation must meet an emission limit of 3.0 lb of VOC per gallon of coating (with a solvent density of 7.36 lb per gallon) or the coater must control VOC emissions to an equivalent level. Assuming that the production rate (solids usage rate), transfer efficiency, and film thickness stay constant, what are the coater's "allowable" hourly VOC emissions?

For the existing coating, the actual VOC emissions are:

$$\frac{10 \text{ gal coating}}{h} \times \frac{5.5 \text{ lb VOC}}{\text{gal coating}} = \frac{55 \text{ lb VOC}}{h}$$

*This example presents a method for determining hourly VOC mass emissions for offset calculations; however, RACT limitations should normally be based on either applicable coating formulations or control efficiency requirements. An hourly cap would normally only be used in addition to these RACT limitations.

The solids usage rate is:

$$\frac{10 \text{ gal coating}}{\text{h}} \times \frac{0.25 \text{ gal solids}}{\text{gal coating}} = \frac{2.5 \text{ gal solids}}{\text{h}}$$

For the complying coating, the VOC (solvent) volume fraction is:

$$\frac{3.0 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal VOC}}{7.36 \text{ lb VOC}} = \frac{0.41 \text{ gal VOC}}{\text{gal coating}}$$

The complying coating solids volume fraction is:

$$1.0 - 0.41 = \frac{0.59 \text{ gal solids}}{\text{gal coating}}$$

Using the solids usage rate calculated above, the gallons of complying coating required are:

$$\frac{2.5 \text{ gal solids}}{\text{h}} \times \frac{\text{gal coating}}{0.59 \text{ gal solids}} = \frac{4.24 \text{ gal complying coating}}{\text{h}}$$

The emissions rate at the existing solids applied rate is:

$$\frac{3.0 \text{ lb VOC}}{\text{gal coating}} \times \frac{4.24 \text{ gal coating}}{\text{h}} = \frac{12.72 \text{ lb VOC}}{\text{h}}$$

- -

5.2 EQUIVALENCY CALCULATIONS FOR A CAN COATING OPERATION

Example 2 -

The RACT equivalence requirements for can coating operations are tabulated in 45 FR 80825, dated December 8, 1980. An analysis of two coatings used in an actual plant is:

		Coating No. 1	Coating No. 2
(1)	Actual pounds of VOC per gallon of coating less water and exempt solvents as applied	5.42	1.09
(2)	Gallons of each coating applied	110	240
(3)	Control efficiency, percent	0.81	--
(4)	Volume percent water and exempt solvents in coatings	--	41.3

(continued)

		Coating No. 1	Coating No. 2
(5)	Volume percent solids	26.4	50.0
(6)	Allowable emission limit, lb VOC/gal coating less water and exempt solvents	2.8	2.8

Calculate the following:

(1) Gallons of solids applied.

(2) Pounds of VOC per gallon of solids.

(3) Pounds of VOC emitted.

(4) Allowable VOC emissions.

Answers:

(1) The gallons of solids applied can be calculated as follows:

Gallons of solids applied = (gallons of coating used) x (volume percent solids) ÷ 100%

(Since the quantity of solids used in the equation appears as a percentage it is necessary to divide by 100%.)

Coating No. 1:

$$110 \text{ gal coating applied} \times \frac{26.4 \text{ gal solids}}{100 \text{ gal coating}} = 29 \text{ gal solids applied}$$

Coating No. 2:

$$240 \text{ gal coating applied} \times \frac{50 \text{ gal solids}}{100 \text{ gal coating}} = 120 \text{ gal solids applied}$$

(2) As noted on Page 10, the pounds of VOC per gallon of solids can be calculated as follows:

$$\frac{\text{lb VOC}}{\text{gal of solids}} = \frac{\text{lb VOC/gal coating less water}}{\frac{\text{volume percent solids}}{\text{100-volume percent water}}}$$

Coating No. 1:

$$\frac{5.42 \text{ lb VOC}}{\text{gal coating less water}} \times \frac{100 \text{ gal coating}}{26.4 \text{ gal solids}} \times \frac{100 - 0 \text{ gal coating less water}}{100 \text{ gal coating}}$$

$$= \frac{20.53 \text{ lb VOC}}{\text{gal solids}}$$

Coating No. 2:

$$\frac{1.09 \text{ lb VOC}}{\text{gal coating less water}} \times \frac{100 \text{ gal coating}}{50.0 \text{ gal solids}} \times \frac{100 - 41.3 \text{ gal coating less water}}{100 \text{ gal coating}}$$

$$= \frac{1.28 \text{ lb VOC}}{\text{gal solids}}$$

(3) The pounds of VOC emitted can be calculated as follows:

$$\frac{\text{lb of VOC}}{\text{gal of solids}} \times \text{gal of solids} \times (1 - \text{overall control efficiency*})$$

Coating No. 1:

$$\frac{20.53 \text{ lb VOC}}{\text{gal solids}} \times 29.0 \text{ gal solids} \times (1 - 0.81) = 113.1 \text{ lb VOC}$$

Coating No. 2:

$$\frac{1.28 \text{ lb VOC}}{\text{gal solids}} \times 120 \text{ gal solids} \times (1 - 0) = 153.6 \text{ lb VOC}$$

(4) The allowable VOC emissions can be calculated as follows:

As calculated in Item (2), the gallons of solids applied for coatings No. 1 and No. 2 were 29 and 120, respectively. Assume that the coater will apply the same volume of solids with a RACT complying coating.

Given: (1) Emission limit: 2.8 lb VOC/gal coating

(2) VOC density: 7.36 lb VOC/gal

*The overall control efficiency is equal to the fraction of total VOC used that is destroyed or recovered by the control system. Overall control efficiency = capture device efficiency x control device efficiency.

Allowable pounds of VOC = gallons of complying coating applied x allowable emission limit,

$$= \frac{\text{gal solids applied (per unit of time)}}{\text{volume fraction solids in complying coating}} \times \frac{2.8 \text{ lb VOC}}{\text{gal coating less water and exempt solvents}}$$

Volume fraction VOC:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal VOC}}{7.36 \text{ lb VOC}} = \frac{0.38 \text{ gal VOC}}{\text{gal coating}}$$

Volume fraction solids:

$$1 - 0.38 \text{ gal coating} = \frac{0.62 \text{ gal solids}}{\text{gal coating}}$$

Allowable pounds of VOC for Coating No. 1:

$$29 \text{ gal solids} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{2.8 \text{ lb VOC}}{\text{gal coating}}$$

$$= 131 \text{ lb VOC}$$

Allowable pounds of VOC for Coating No. 2:

$$120 \text{ gal solids} \times \frac{\text{gal coating}}{0.62 \text{ gal solids}} \times \frac{2.8 \text{ lb VOC}}{\text{gal coating}}$$

$$= 542 \text{ lb VOC}$$

Table 2 shows the calculation sequence.

TABLE 2. SUGGESTED FORMAT FOR DETERMINING COMPLIANCE FOR CAN COATING OPERATIONS.

	Lb VOC/ gal coating less water (a)*	Volume % solids (b)*	Volume % solvent (c)	Volume % water (d)*	Lb VOC/ gal solids[1] (e)	Application rate (gal/ units produced (f)*	Units produced (g)*	Gal coating applied (f x g) (h)	Gal solids applied (b x h ÷ 100) (i)	Overall Add-on Control efficiency[2] (j)*	Lb of VOC [e x i] (i - j) (k)
Actual Emissions[3]											
Sheet coating	5.42	26.4	-	0	20.52	22	5	110	29.0	0.81	113.0
Sheet coating	1.09	50.0	-	41.3	1.28	10	24	240	120.0	-	153.0
Sheet coating	5.06	31.2	-	0	16.23	10	24	240	74.9	0.81	231.0
Side seam	6.34	13.9	-	0	45.59	1.5	18	27	3.8	-	173.8
Inside spray	3.91	16.0	-	65.9	8.33	8	24	192	30.7	-	255.7
End compound	4.20	42.9	-	0	9.80	1.5	24	36	15.4	-	150.0
ACTUAL TOTAL EMISSIONS											1,077.5
Allowable Emissions Using Complying Coating[4]											
Sheet coating	2.8	62.0	38.0	-	4.52	9.4	5	47	29.0	-	131.0
Sheet coating	2.8	62.0	38.0	-	4.52	8.1	24	194	120.0	-	542.0
Sheet coating	2.8	62.0	38.0	-	4.52	5.0	24	121	74.9	-	338.0
Side seam	5.5	25.3	74.7	-	21.76	0.8	18	15	3.8	-	82.7
Inside spray	4.2	42.9	57.1	-	9.78	3.0	24	72	30.7	-	300.2
End compound	3.7	49.7	50.3	-	7.44	1.3	24	31	15.4	-	114.6
ACTUAL TOTAL EMISSIONS											1,509.5

*Note: Data in columns a, b, d, f, g, and j (under actual emissions) were obtained from plant records including thinning solvent. Data in columns a, b, and d were determined using procedures in the VOC Data Sheets.

[1]For actual coatings, $e = \frac{a}{(\frac{b}{100 - d})}$

For complying coatings, $e = \frac{a}{1 - \frac{a}{D}}$

TABLE 2. (continued)

D = Presumed density of VOC for complying coating (7.36 lb/gal).

[2]Control efficiency varies with emission control devices used. The percent capture and control efficiency must be established by using approved test methods. The source must always maintain process and control system parameters as close as possible to those used in the original capture and control efficiency demonstration. If there are any significant changes in these parameters, the source must make a new capture and/or control efficiency demonstration as deemed appropriate by the compliance authority.

[3]Concept based on the following principal for comparing actual and allowable emissions: lb VOC emitted = lb VOC/gal of solids x gal of solids applied per unit. (Same gal of solids applied for actual and allowable emissions.)

[4]Complies with State VOC emission limitations.

SECTION 6

COMPLEX CALCULATIONS

This section presents example calculations demonstrating situations that may require a series of calculations.

6.1 COMPLIANCE DETERMINATION FOR AUTO PLANT PRIMER-SURFACER (GUIDE COAT) OPERATION

Example 1 -

An auto primer-surfacer operation uses a coating that contains 3.58 lb VOC/gal of coating with a transfer efficiency of 50 percent. The RACT emission limit is 2.8 lb VOC/gal of coating less water at 30 percent transfer efficiency (waterborne equivalence). Is the operation in compliance?

Given: (1) The manufacturer's data show that the undiluted coating has 50.0 volume percent solids.

(2) The plant adds 0.05 gal of thinner blend per gallon of undiluted coating:

(a) 0.02 gallon of thinner No. 1/gallon undiluted coating (thinner density 7.36 lb/gal).

(b) 0.02 gallon of thinner No. 2/gallon undiluted coating (thinner density 5.43 lb/gal).

(c) 0.01 gallon of thinner No. 3/gallon undiluted coating (thinner density 9.52 lb/gal).

(3) The density of the undiluted coating is 10.25 lb/gal.

(4) Weight fraction of VOC in undiluted coating =

$$\frac{0.333 \text{ lb VOC solvent}}{\text{lb undiluted coating}}$$

First, verify the VOC content of the coating. In order to do this, the VOC content of the undiluted coating and the thinners must be calculated. The mass of VOC in the undiluted coating is:

$$\frac{0.333 \text{ lb VOC}}{\text{lb undiluted coating}} \times \frac{10.25 \text{ lb undiluted coating}}{\text{gal undiluted coating}} = \frac{3.41 \text{ lb VOC}}{\text{gal undiluted coating}}$$

The mass of thinner added per gallon of undiluted coating is:

$$\frac{0.02 \text{ gal thinner No. 1}}{\text{gal undiluted coating}} \times \frac{7.36 \text{ lb thinner No. 1}}{\text{gal thinner No. 1}} + \frac{0.02 \text{ gal thinner No. 2}}{\text{gal undiluted coating}}$$

$$\times \frac{5.43 \text{ lb thinner No. 2}}{\text{gal thinner No. 2}} + \frac{0.01 \text{ gal thinner No. 3}}{\text{gal undiluted coating}} \times \frac{9.52 \text{ lb thinner No. 3}}{\text{gal thinner No. 3}}$$

$$= 0.147 + 0.109 + 0.095 = \frac{0.351 \text{ lb thinner}}{\text{gal undiluted coating}}$$

The mass VOC per volume coating at application is:

$$\frac{3.41 \text{ lb VOC/gal undiluted coating} + 0.351 \text{ lb thinner/gal undiluted coating}}{1.05 \text{ gal coating/gal undiluted coating}}$$

$$= 3.58 \text{ lb VOC/gal coating}$$

The undiluted coating has 50.0 volume percent solids. After the coating is diluted with 0.05 gallon of thinner per gallon of coating, the volume percent solids is:

$$\frac{0.50}{1 + 0.05} = \frac{0.48 \text{ gal solids}}{\text{volume coating}}$$

The equivalency calculations must be made on a solids basis. The formula for determining the maximum allowable emissions on a solids basis is:

$$\text{Allowable emissions} = \frac{\text{allowable mass of VOC per volume coating}}{(\text{baseline TE})\ (\text{baseline volume solids})}$$

As noted in earlier examples, an assumed VOC density of 7.36 gal is used to calculate the volume solids content of the "presumptive" RACT coating.

The volume of VOC in the "presumptive" RACT coating is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal VOC}}{7.36 \text{ lb VOC}} = \frac{0.38 \text{ gal VOC}}{\text{gal coating}}$$

Therefore, the baseline volume of solids is:

$$1 - 0.38 = \frac{0.62 \text{ gal solids}}{\text{gal coating}}$$

Allowable emissions are:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids}}{0.30 \text{ gal solids applied}} = \frac{15.1 \text{ lb VOC}}{\text{gal solids applied}}$$

The formula for actual emissions is:

$$\text{Actual emissions} = \frac{\text{actual mass VOC per volume coating}}{(\text{actual \% TE})\left(\frac{\text{actual volume solids}}{\text{gal coating}}\right)}$$

The actual mass of VOC per volume coating is 3.58 lb VOC/gallon coating. The actual transfer efficiency is 50 percent. The actual volume of solids in the sprayed coating is 48 percent.

Actual emissions are:

$$\frac{3.58 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.48 \text{ gal solids}} \times \frac{1 \text{ gal solids}}{0.50 \text{ gal solids applied}} = \frac{14.9 \text{ lb VOC}}{\text{gal solids applied}}$$

Actual emissions (14.9 lb VOC per gallon of solids applied) are less than the maximum allowable emissions (15.1 lb VOC per gallon of solids applied); therefore, the operation is in compliance.

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6.2 DETERMINING COMPLIANCE FOR A LARGE APPLIANCE COATING LINE USING SEVERAL TYPES OF SPRAY EQUIPMENT

Example 2 -

A large appliance manufacturer has a coating operation that employs electrostatic spray coating equipment and manual spray coating equipment. The following data are available regarding the operation. Determine the compliance status. If the large appliance manufacturer is out of compliance, what percent reduction is required to achieve compliance?

	(A) Electrostatic coating	(B) Manual coating
Transfer efficiency, percent	90	40
Average volume percent of solids in coating	39	39
VOC content, lb VOC/gal coating less water	4.5	4.5
Gallons of coating used per day	30.4	47.1
Emission limit, lb/gallon less water	2.8	2.8
Baseline transfer efficiency for large appliances, percent	60	60

The baseline transfer efficiency is 60 percent for a large appliance coater. Table 3 is a tabulation of the available data and calculation results. The actual calculations follow.

TABLE 3. LARGE APPLIANCE MULTITRANSFER EFFICIENCY CALCULATION.

Spray type	Gallons of coating/day	Solids, vol. %	Lb VOC/ gallon coating	Lb VOC/ gallon solids	% TE	Lb VOC/gallon solids applied	Gallons of solids applied/day	Pounds of VOC/day
				Actual emissions				
A	30.4	39	4.5	11.5	90	12.8	10.7	136.8
B	47.1	39	4.5	11.5	40	28.8	7.3	212.0
Total								348.8
				Allowed emissions				
A	28.8	62	2.8	4.5	60	7.5	10.7	80.6
B	19.6	62	2.8	4.5	60	7.5	7.3	54.9
Total								135.5

Under the actual emissions category, the following calculations can be made.

For A and B, the mass of VOC per volume of solids is:

$$\frac{4.5 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.39 \text{ gal solids}} = \frac{11.5 \text{ lb VOC}}{\text{gal solids}}$$

For A, the mass of VOC per volume of solids applied is:

$$\frac{4.5 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.39 \text{ gal solids}} \times \frac{1 \text{ gal solids}}{0.90 \text{ gal solids applied}} = \frac{12.82 \text{ lb VOC}}{\text{gal solids applied}}$$

For B, the mass of VOC per volume of solids applied is:

$$\frac{4.5 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.39 \text{ gal solids}} \times \frac{1 \text{ gal solids}}{0.40 \text{ gal solids applied}} = \frac{28.85 \text{ lb VOC}}{\text{gal solids applied}}$$

For A, the volume of solids applied per day is:

$$\frac{30.4 \text{ gal coating}}{\text{day}} \times \frac{0.39 \text{ gal solids}}{\text{gal coating}} \times \frac{0.90 \text{ gal solids applied}}{\text{gal solids used}} = \frac{10.7 \text{ gal solids applied}}{\text{day}}$$

For B, the volume of solids applied per day is:

$$\frac{47.1 \text{ gal coating}}{\text{day}} \times \frac{0.39 \text{ gal solids}}{\text{gal coating}} \times \frac{0.40 \text{ gal solids applied}}{\text{gal solids used}} = \frac{7.3 \text{ gal solids applied}}{\text{day}}$$

For A, the mass of VOC emissions per day is:

$$\frac{4.5 \text{ lb VOC}}{\text{gal coating}} \times \frac{30.4 \text{ gal coating}}{\text{day}} = \frac{136.8 \text{ lb VOC}}{\text{day}}$$

For B, the mass of VOC emissions per day is:

$$\frac{4.5 \text{ lb VOC}}{\text{gal coating}} \times \frac{47.1 \text{ gal coating}}{\text{day}} = \frac{212.0 \text{ lb VOC}}{\text{day}}$$

Under the allowed emissions category, the following calculations can be made.

For A and B, the volume fraction of VOC in the baseline coating is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal VOC}}{7.36 \text{ lb VOC}} = \frac{0.38 \text{ gal VOC}}{\text{gal coating}}$$

The volume fraction solids in the coating is:

$$1 - \frac{0.38 \text{ gal VOC}}{\text{gal coating}} = \frac{0.62 \text{ gal solids}}{\text{gal coating}}$$

The baseline mass of VOC per volume solids is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} = \frac{4.5 \text{ lb VOC}}{\text{gal solids}}$$

For A and B, the maximum allowable emissions are:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.60 \text{ gal solids applied}} = \frac{7.5 \text{ lb VOC}}{\text{gal solids applied}}$$

The volume of solids applied remains the same. Therefore, for A, the gallons of complying coating used per day would be:

$$\frac{10.7 \text{ gal solids applied}}{\text{day}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.6 \text{ gal solids applied}}$$

$$= \frac{28.8 \text{ gal coating}}{\text{day}}$$

For B, the gallons of complying coating used per day would be:

$$\frac{7.3 \text{ gal solids}}{\text{day}} \times \frac{1 \text{ gal coating}}{0.62 \text{ gal solids}} \times \frac{1 \text{ gal solids used}}{0.6 \text{ gal solids applied}} = \frac{19.6 \text{ gal coating}}{\text{day}}$$

For A, the mass of VOC emissions allowed per day is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{28.8 \text{ gal coating}}{\text{day}} = \frac{80.6 \text{ lb VOC}}{\text{day}}$$

For B, the mass of VOC emissions allowed per day is:

$$\frac{2.8 \text{ lb VOC}}{\text{gal coating}} \times \frac{19.6 \text{ gal coating}}{\text{day}} = \frac{54.9 \text{ lb VOC}}{\text{day}}$$

The total actual VOC emissions from A and B are 348.8 lb VOC per day. The total allowable VOC emissions are 135.5 lb VOC per day. Therefore, the operation is out of compliance. To achieve compliance, the required reduction in emissions is:

$$\frac{348.8 - 135.5}{348.8} \times 100 = 61 \text{ percent}$$

SECTION 7

GRAPHS AND TABLES USEFUL IN APPROXIMATING AND DOUBLE-CHECKING SURFACE COATING CALCULATIONS

Figure 1 can be used to evaluate compliance alternatives for waterborne and organic-borne coatings. This can be done by drawing a horizontal line from the required VOC content of coating (less water and exempt solvents) to the appropriate curve (depending on ratio of water to organic solvent in coating). A vertical line is then drawn from the point of intersection to the x-axis which yields the volume percent solids. All of the coatings represented by the horizontal line have the same pounds of VOC solvent per gallon of coating (less water and exempt solvents). A vertical line in Figure 1 from the volume percent solids to the organic-borne line represents all of the coatings with the same volume percent solids. Horizontal lines drawn from the appropriate waterborne curves yield the VOC contents of the coatings less water and exempt solvents. Note that these values are considerably different for coatings with the same solids contents.

Figures 2 and 3 are the same graph, only Figure 2 is drawn to a larger scale. If the pounds of VOC solvent per gallon of coating (less water and exempt solvents) is known, these figures can be used to approximate the pounds of VOC solvent per gallon of coating solids, assuming a solvent density of 7.36 pounds per gallon.

Table 4 presents volume percent solids equivalency data for different coating operations. Table 5 presents CTG Equivalency Data. A VOC density of 7.36 pounds per gallon is assumed in these tables. Table 6 provides equivalent solids deposited limits. Table 7 presents some useful conversion factors.

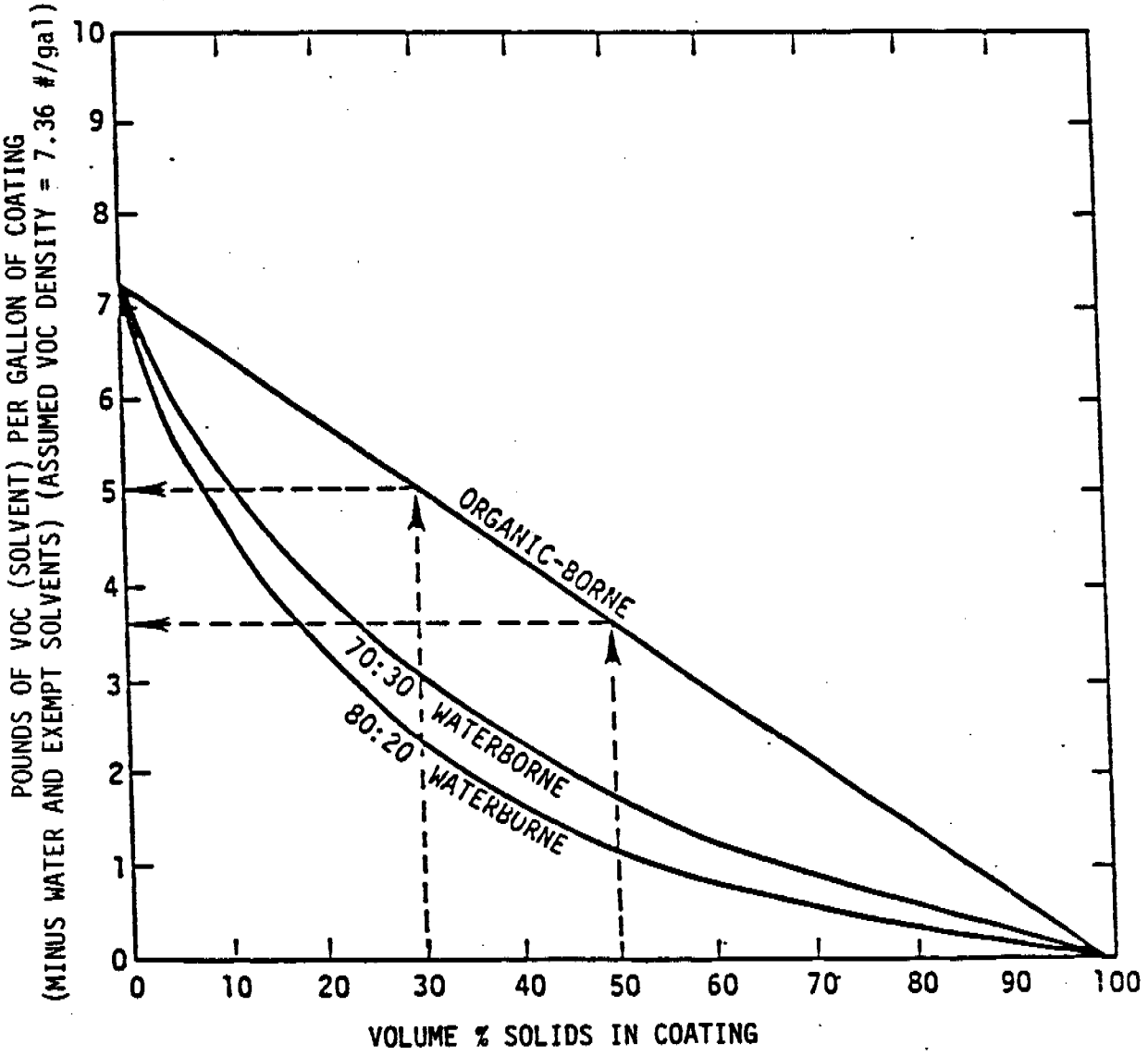


Figure 1. Graph for determining equivalent solids/VOC (solvent) contents of waterborne and organic-borne coatings.

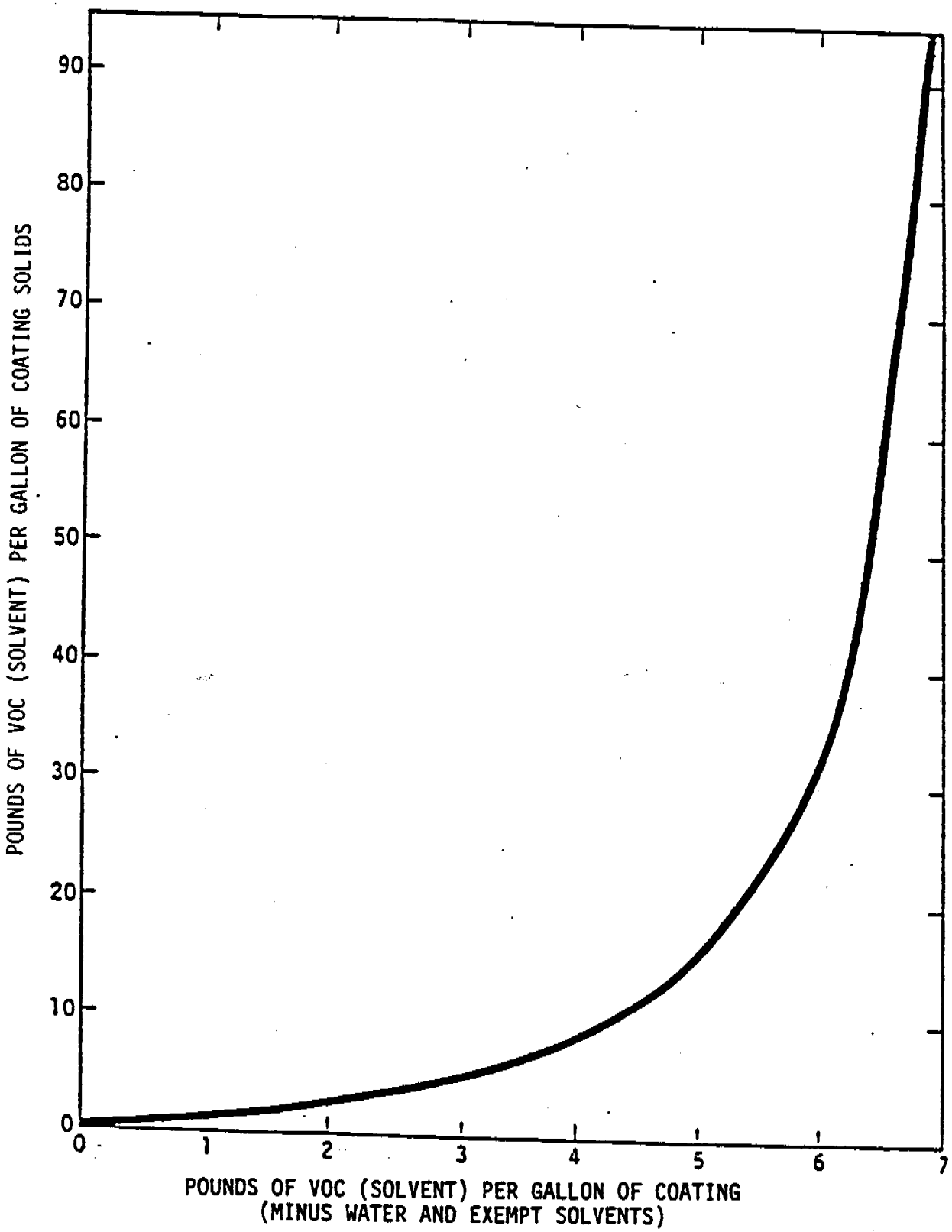


Figure 2. Graph for determining pounds of VOC (solvent) per gallon of coating solids.

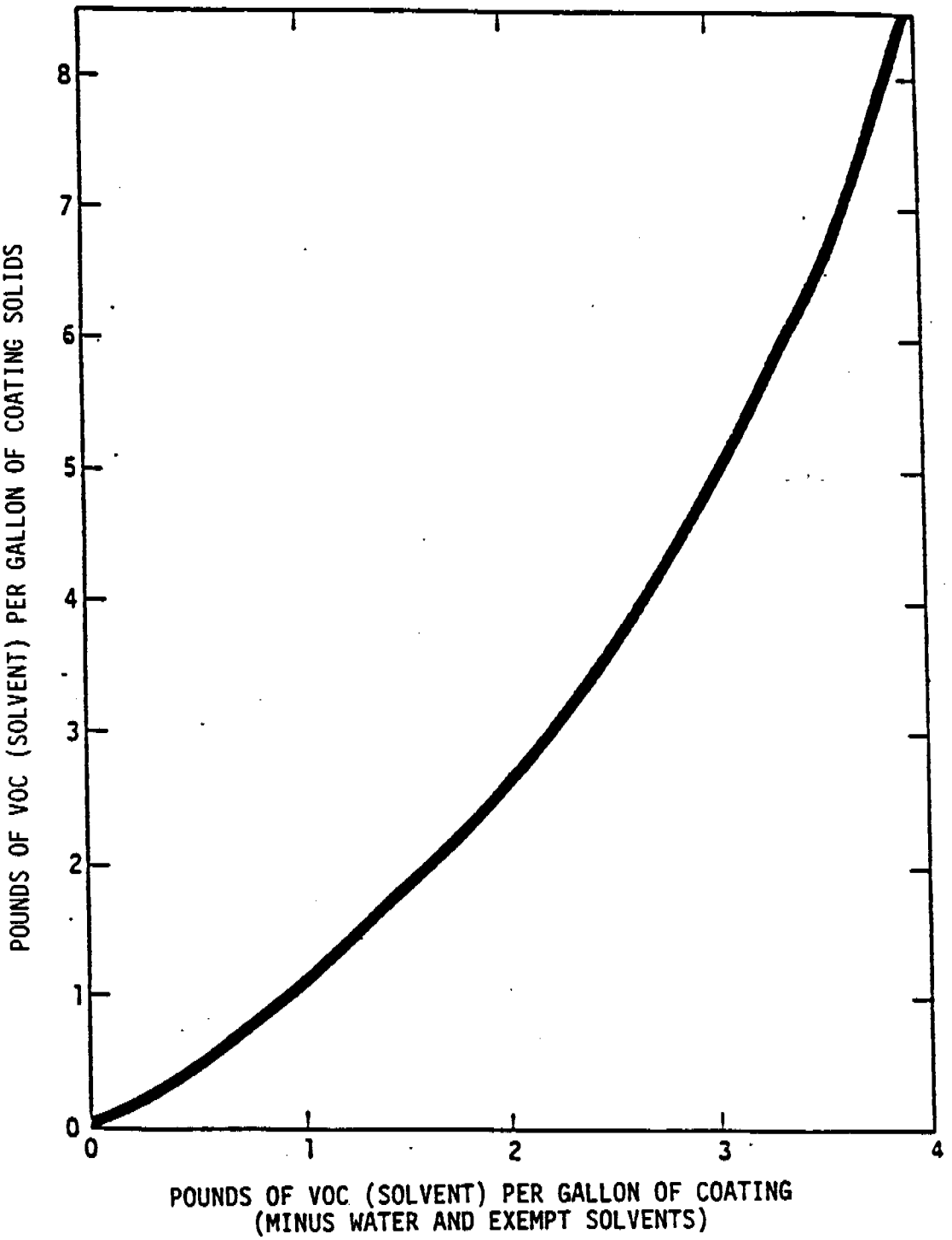


Figure 3. Smaller-scale graph for determining pounds of VOC (solvent) per gallon of coating solids.

TABLE 4. CTG VOLUME PERCENT SOLIDS EQUIVALENCY DATA

Industrial finishing categories	Kg VOC per liter of coating less water	Lb VOC per gallon of coating less water	Solvent-borne coating equivalent volume % solids
CAN INDUSTRY			
Sheet basecoat (exterior and interior) and over-varnish; two-piece can exterior (basecoat and over-varnish)	0.34	2.8	62.0
Two- and three-piece can interior body spray, two-piece can exterior end (spray or roll coat)	0.51	4.2	42.9
Three-piece can side-seam spray	0.66	5.5	25.3
End sealing compound	0.44	3.7	49.7
COIL COATING			
Prime and topcoat or single coat operation	0.31	2.6	64.7
FABRIC COATING			
Fabric coating line	0.35	2.9	60.6
Vinyl coating line	0.45	3.8	48.4
PAPER COATING			
Coating line	0.35	2.9	60.6
AUTOMOTIVE AND LIGHT-DUTY TRUCK ASSEMBLY PLANT			
Primer (electrodeposited) application, flashoff area and oven	0.14	1.2	83.7
Surfacer (guide-coat) application, flashoff area and oven	0.34	2.8	62.0
Topcoat application, flashoff area and oven	0.34	2.8	62.0

(continued)

TABLE 4. (continued)

Industrial finishing categories	Kg VOC per liter of coating less water	Lb VOC per gallon of coating less water	Solvent-borne coating equivalent volume % solids
AUTOMOTIVE AND LIGHT-DUTY TRUCK ASSEMBLY PLANT (continued)			
Final repair application, flashoff area and oven	0.58	4.8	34.8
METAL FURNITURE			
Coating line	0.36	3.0	59.2
MAGNET WIRE INSULATION			
Wire coating oven	0.20	1.7	76.9
LARGE APPLIANCES			
Prime, single, or topcoat application area, flashoff area and oven	0.34	2.8	62.0
MISCELLANEOUS METAL PARTS			
Air-dried items	0.42	3.5	52.4
Clear-coated items	0.52	4.3	41.6
Frequent-color-change items	0.36	3.0	59.2
Powder-coated items	0.05	0.4	94.6
Extreme performance coatings	0.42	3.5	52.4

TABLE 5. CTG EQUIVALENCY DATA (VOC DENSITY = 7.36 LB/GAL)

Industrial finishing categories	Solvent-borne coating equivalent volume % solids	Lb VOC per gallon of coating less water	Kg VOC per liter of coating less water	Lb VOC per gallon of solids	Kg VOC per liter of solids
Can Industry					
Sheet basecoat (exterior and interior) and over-varnish; two-piece can exterior (base-coat and over-varnish)	62.0	2.8	0.34	4.5	0.55
Two- and three-piece can interior body spray, two-piece can exterior end spray or roll coat	42.9	4.2	0.51	9.8	1.19
Three-piece can side-seam spray	25.3	5.5	0.66	21.7	2.61
End sealing compound	50.3	3.7	0.44	7.4	0.88
Coil Coating					
Prime and topcoat or single coat operation	64.7	2.6	0.31	4.0	0.48
Fabric Coating					
Fabric coating line	60.6	2.9	0.35	4.8	0.58
Vinyl coating line	48.4	3.8	0.45	7.9	0.93

(continued)

TABLE 5. (continued)

Industrial finishing categories	Solvent-borne coating equivalent volume % solids	Lb VOC per gallon of coating less water	Kg VOC per liter of coating less water	Lb VOC per gallon of solids	Kg VOC per liter of solids
Paper Coating					
Coating line	60.6	2.9	0.35	4.8	0.58
Automotive and Light-Duty Truck Assembly Plant					
Primer (electrodeposition) application, flashoff area and oven	83.7	1.2	0.14	1.4	0.17
Surfacer (guide coat) application, flashoff area and oven	62.0	2.8	0.34	4.5	0.55
Topcoat application, flashoff area and oven	62.0	2.8	0.34	4.5	0.55
Final repair application, flashoff area and oven	34.8	4.8	0.58	13.8	1.67
Metal Furniture					
Coating line	59.2	3.0	0.36	5.1	0.61
Magnet Wire Insulation					
Wire coating oven	6.9	1.7	0.20	2.2	0.26

(continued)

TABLE 5. (continued)

Industrial finishing categories	Solvent-borne coating equivalent volume % solids	Lb VOC per gallon of coating less water	Kg VOC per liter of coating less water	Lb VOC per gallon of solids	Kg VOC per liter of solids
Large Appliances					
Prime, single, or topcoat application area, flashoff area and oven	62.0	2.8	0.34	4.5	0.55
Miscellaneous Metal Parts and Products					
Air-dried items	52.4	3.5	0.42	6.7	0.80
Clear-coated items	41.6	4.3	0.52	10.3	1.25
Frequent-color-change items	59.2	3.0	0.36	5.1	0.61
Powder-coated items	95.6	0.4	0.05	0.4	0.05
Extreme performance coatings	52.4	3.5	0.42	6.7	0.80

TABLE 6. EQUIVALENT CTG SOLIDS DEPOSITED LIMITS

	Lb/gal-H_2O (kg/l)	Volume % Solids	Baseline T.E.	Lb/gal solids deposited (kg/l)
Auto and Light-duty Truck*				
Surfacer	2.8 (0.34)	62.0	30	15.1 (1.83)
Topcoat	2.8 (0.34)	62.0	30	15.1 (1.83)
Metal Furniture				
Coating line	3.0 (0.36)	59.2	60	8.4 (1.01)
Large Appliances				
Coating Line	2.8 (0.34)	62.0	60	7.5 (0.91)

*Waterborne equivalence

TABLE 7. METRIC CONVERSION FACTORS

A.

Metric abbrevation	Metric unit	Equivalent English unit
kg	kilogram (10^3 grams)	2.2046 lb
liter	liter	0.2642 gal, 0.353 ft^3
Mg	megagram (10^6 grams)	2,204.6 lb
MT	metric ton (10^6 grams)	2,204.6 lb
dscm	dry standard cubic meters	35.31 dry st. ft^3
scmm	standard cubic meter per min	35.31 ft^3/min

B. Multiply lb/gal x 0.12 to get kg/liter

C. Multiply kg/liter x 8.34 to get lb/gal

D. Temperature: Degrees Celsius or centigrade (°C) can be converted to degrees Fahrenheit (°F) by the following forumla:

$$t°F = 1.8\ (t°C) + 32$$

REFERENCES

1. "Compliance with VOC Emission Limitations for Can Coating Operations," 45 FR 80824, dated December 8, 1980.

2. "Glossary for Air Pollution Control of Industrial Coating Operations." Second Edition. Emission Standards and Engineering Division, U.S. Environmental Protection Agency. EPA-450/3-83-013R. December 1983.

3. Memorandum entitled "Appropriate Transfer Efficiencies for Metal Furniture and Large Appliace Coating," from G.T. Helms, Chief, Control Programs Operations Branch, to Chief, Air Programs Branch, Regions I-X, dated November 28, 1980.

4. Memorandum entitled "Appropriate Transfer Efficiency for Water-Borne Equivalence," from R.G. Rhoads, Director, Control Programs Development Division to Director, Air and Hazardous Materials Division, Regions I-X, dated July 3, 1979.

5. Memorandum entitled "Determination of Capture Efficiency," from J. Berry, Chief, Chemical Analysis Section, to D. Cook, EPA Region IV, dated July 7, 1980.

6. Memorandum entitled "Equivalency Calculations with the CTG Recommendations for Surface Coating," from R.G. Rhoads, Director, Control Programs Development Division, to David Kee, Director, Air and Hazardous Materials Division, Region V, dated October 17, 1980.

7. Memorandum entitled "Procedure to Calculate Equivalency with the CTG Recommendations for Surface Coating, from R.G. Rhoads, Director, Control Programs Development Division, to Chief, Air Programs Branch, Regions I-X, dated May 5, 1980.

8. Memorandum entitled "RACT Options for Can Coating Operations," from R.G. Rhoads, Director, Control Programs Development Division to Director, Air and Hazardous Materials Division, Regions I-X, dated November 21, 1978.

9. Memorandum entitled "Role of Improved Transfer Efficiency in Demonstrating Compliance with the CTG Recommendations for Surface Coating", from G.T. Helms, Chief, Control Programs Operations Branch, to W.S. Baker, Chief, Air Programs Branch, Region II, dated December 2, 1980.

10. "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings." Emission Standards and Engineering Division, U.S. Environmental Protection Agency. EPA-450/3-84-019. December 1984.

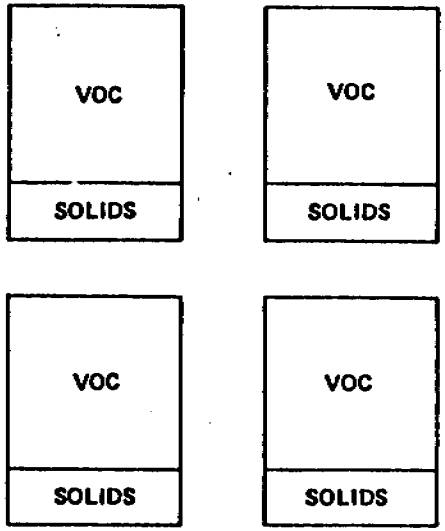
APPENDIX A

GLOSSARY OF TERMS USED IN
AIR POLLUTION CONTROL OF EMISSIONS
FROM INDUSTRIAL COATING OPERATION
EPA PUBLICATION NO. 450/3-83-013R, PAGES 26-29

- HOW MUCH COATING IS NEEDED TO DO A PARTICULAR JOB?

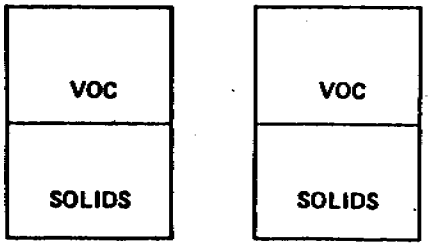
The same volume of coating solids must be deposited on an object to coat it to a desired film thickness regardless of the type of coating or volatile organic compound content of the coating used. Solids make the film. Volatiles (VOC, water, and non-photochemically reactive solvents) evaporate.

Four gallons of a 25 volume percent (v/o) solids coating must be used to get one gallon of coating solids.



A-3

But, only two gallons of a 50 v/o solids coating must be used to get one gallon of coating solids.

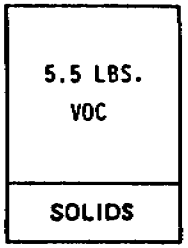


This means that twice as much work can be done with a gallon of 50 v/o solids coating than with a gallon of 25 v/o solids coating. Twice as many gallons of 25 percent solids coating are needed than gallons of 50 percent solids coating to do the same job.

- HOW DO EMISSIONS FROM DIFFERENT COATINGS COMPARE?

Comparisons of the percent difference in emissions between two coatings, or between a coating and an emission limit, must be done on a solids basis.

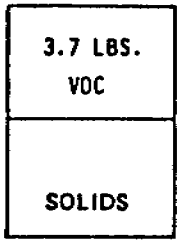
Each gallon of the 25 v/o solids coating contains 5.5 pounds of VOC.



So, for each gallon of coating solids, 22.0 pounds of VOC are emitted.

$$\frac{5.5 \text{ pounds VOC}}{\text{gallon coating}} \times \frac{4 \text{ gallons coating}}{\text{gallon solids}}$$

Each gallon of the 50 v/o solids coating contains 3.7 pounds of VOC.



So, for each gallon of coating solids, 7.4 pounds of VOC are emitted.

$$\frac{3.7 \text{ pounds VOC}}{\text{gallon coating}} \times \frac{2 \text{ gallons coating}}{\text{gallon solids}}$$

Thus, emissions from the 50 v/o solids coatings are 66 percent less than from the 25 v/o solids coating when providing an equal amount of solids to the process.

$$\frac{22.0 - 7.4}{22.0} = 0.66$$

- WHAT EMISSION REDUCTION IS NEEDED TO MEET AN EMISSION LIMIT?

This calculation, which must also be done on a solids basis, is the same as that used above to compare emissions from two different coatings.

A coater who uses a 25 v/o solids coating containing 5.5 pounds of VOC per gallon, less water, must reduce emissions by 66 percent to meet an emission limit of 3.7 pounds of VOC per gallon, less water.

- HOW MUCH DO IMPROVEMENTS IN TRANSFER EFFICIENCY HELP A SOURCE TO COMPLY?

The coater may want to use a coating that does not comply with a regulation and compensate by improvements in the transfer efficiency with which the coating is applied to meet an equivalent emission level. In order to calculate credit for VOC reductions which result from improvements in transfer efficiency, calculations should be done using units of:

$$\frac{\text{lb VOC}}{\text{gallon solids deposited}}$$

These units are determined by dividing lb VOC/gallon solids by the transfer efficiency expressed as a decimal fraction. For example, if the starting transfer efficiency is 60 percent, the units would be:

$$\frac{\text{lb VOC}}{\text{gal solids deposited (with the old system)}} = \frac{\text{lb VOC}}{\text{gal solids in coating used}} \times \frac{1.0 \text{ gal solids in coating used}}{0.60 \text{ gal solids deposited}}$$

If the same paint were now to be sprayed with 90 percent transfer efficiency, the new value would be:

$$\frac{\text{lb VOC}}{\text{gallon solids deposited (with new system)}} = \frac{\text{lb VOC}}{\text{gallon solids in coating used}} \times \frac{1.0 \text{ gal solids in coating used}}{0.90 \text{ gal solids deposited}}$$

If both the solvent content of the coating and the transfer efficiency are changed, the situation becomes:

$$\frac{\text{lb VOC}}{\text{gal solids deposited (with new paint and new transfer efficiency)}} = \frac{\text{lb VOC}}{\text{gal solids in new coating used}} \times \frac{1.0 \text{ gal solids in new coating used}}{T \text{ gal solids deposited}}$$

where T = the new transfer efficiency expressed as a decimal

Expressed in these units, the emissions from the old and new systems can be directly compared to determine the reduction achieved.

NOTE: For metal furniture and appliance coating, the EPA has recommended* that credit for transfer efficiency be given from a baseline of 60 percent transfer efficiency (TE). For example, if a company goes from 35 percent TE to 85 percent TE, credit should only be given for going from 60 percent TE to 85 percent TE to avoid rewarding a source that has historically had poor transfer efficiency - hence a high emission rate.

The rationale for this is that 60 percent TE is a reasonable transfer efficiency to achieve for these industries, and credit should only be given for exceeding 60 percent TE.

For the automobile industry, the CTG recommendation for baseline transfer efficiency is 30 percent TE for both primer surfacer and topcoat. This is the efficiency at which waterborne coatings were applied at two existing assembly plants.

* Memo from G. T. Helms, Chief, Control Programs Operations Branch, EPA, to Chief, Air Programs Branch, EPA Regions I-X, "Appropriate Transfer Efficiencies for Metal Furniture and Large Appliance Coating", November 28, 1980.

APPENDIX B

PROCEDURES FOR CERTIFYING QUANTITY OF VOLATILE ORGANIC COMPOUNDS EMITTED BY PAINT, INK, AND OTHER COATINGS

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-84-019
December 1984

Air

EPA

Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings

NOTICE

THIS EDITION INCLUDES PAGES III-4
AND III-9 AS REVISED JUNE 19,1986

EPA-450/3-84-019

Procedure for Certifying Quantity of Volatile Organic Compounds Emitted By Paint, Ink, and Other Coatings

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1984

This report has been reviewed by the Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Copies of this report are available through the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711, or from the National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

PREFACE

This manual was conceived as a way to provide simple step-by-step instructions for certifying the quantity of volatile organic compounds (VOC) that will be released by a coating. It has not turned out that way. The guidance is here, but in spite of great diligence, the instructions remain imposing.

The manual was prepared for several reasons. First, the coatings industry, as represented by the National Paint and Coatings Association, had requested a certification procedure which would relieve their customers the expense of analysis. Second, the complexity of the calculations necessary to determine compliance, for example, when dilution solvent is added to a coating, continue to confound Federal, State and Local enforcement personnel. Finally, results of a recent review of the Agency's reference method for determining VOC reemphasized the importance of analytical procedures to verify VOC content.

In response to the results of the review of the test methods, this manual reaffirms that Reference Method 24 or its constituent methods developed by the American Society for Testing and Materials (ASTM), are the procedures by which the VOC content of a coating will be determined for compliance with Federal regulations. The earliest guidance was not so specific. In 1977, the first report[1], written to assist States in developing regulations for sources of VOC emissions, provided recommendations for the maximum allowable VOC content for complying coatings in a variety of industries. These values were expressed in mass of VOC per unit volume of coating. In deriving the recommended limitation, the VOC content of a coating was calculated based on the solids content provided by the coating manufacturer. The Agency calculated the mass of VOC in the coating by assuming the VOC had a density of 7.36 pounds per gallon.

Solvent and VOC were used somewhat interchangebly even though it was recognized that organics such as resin monomer, oligimers, and reaction by-products could be released by a coating during the cure. There was no accepted analytical method available for measuring the total VOC which would be released by a coating. The initial guidance[1] provided an analytical method for use only for air-dry coatings, those where all VOC emissions would be expected to come as a result of evaporation of solvent. On a volume basis, air dry coatings constituted the largest catagory of coatings then in use.

The Agency subsequently developed a more general analytical procedure that could be used to determine the total VOC in a coating. On October 3, 1980, the Agency published "Reference Method 24 (RM-24) -

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[1]Control of Volatile Organic Emissions from Stationary Sources - Volume II: Surface Caoting of Cans, Coils, Paper Fabrics, Automobiles, and Light-duty Trucks, Document No. EPA-450/2-77-008

Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings," in the Federal Register (45 FR 65958). For the first time the Agency formally specified an analytical method for the VOC content of those coatings that cure by chemical reaction. Even then, the announcement continued to allow the manufacturer's formulation to be used to calculate the VOC content but specified that the analytical technique, RM-24, would be the reference in any conflict between the two.

During 1981 and 1982, as more State and Federal regulations were established, the demand for low-solvent coatings began a continuing increase in the sales volume of reaction-cure coatings. There was some concern voiced by the industry in how appropriate the reference method was for these type coatings. To find out, the Agency began a review of RM-24 to determine the effect of temperature and exposure time on the indicated VOC "content". It was concluded that the maximum effect of those time-temperature combinations that were examined amounted to only about a 10 percent variation. Somewhat more surprising was that the solvent sometimes accounted for only 50 to 70 percent of the total VOC measured by the reference method.

The obvious conclusion was that RM-24 is a better measure of the total organics freed by a coating than is the solvent. This manual implements a policy based on that conclusion. Certification of VOC content on the attached Data Sheets must be based on an analysis using RM-24. No longer will solvent content be permitted as a surrogate for VOC unless a showing is first made that its use is a reasonable alternative or equivalent method of determining the VOC content of that particular coating.

One final comment. Since VOC is not always synonomous with solvent, it follows that the amount of solids in a coating cannot be obtained by subtracting the solvent from the total volume of coating. The original Federal Register proposal for RM-24, published on October 3, 1980, recommended the American Society of Test Materials test Number D2697 as the appropriate method of determining solids content. Subsequent comments from the industry maintained that this test is unreliable. As a result, when promulgated in 1980, RM-24 specified that the solids content of a coating can be obtained only from the manufacturer's formulation of the coating.

Dennis Crumpler

Dennis Crumpler
December 14, 1984

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GLOSSARY OF TERMS

"As Applied"	the condition of a coating after dilution by the user just prior to application to the substrate.
"As Supplied"	the condition of a coating before dilution, as sold and delivered by the coating manufacturer to the user.
$(D_c)_a$	coating density "as applied"
$(D_c)_s$	coating density, "as supplied"
D_d	density of dilution solvent
$D_d^{\dagger}$	density of organic solvent/water mixture
D_w	density of water (8.33 lb/gal)
R_d	dilution solvent ratio, equals the volume of VOC added per unit volume of coating "as supplied"
$R_d^{\dagger}$	equals the volume of premixed water and VOC added per unit volume of coating "as supplied"
$(V_n)_a$	Volume percent solids of coating "as applied"
$(V_n)_s$	Volume percent solids of coating "as supplied"
$(VOC)_a$	VOC content of "as applied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(VOC)_s$	VOC content of "as supplied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(V_w)_a$	the water content, in volume percent, of coating "as applied"
$(V_w)_d$	the water content, in volume percent, of the dilution solvent added to the "as supplied" coating
$(V_w)_s$	the water content, in volume percent, of the coating "as supplied"
$(W_o)_a$	the organic volatile content, in weight percent, of the coating "as applied"
$(W_o)_s$	the organic volatile content, in weight percent, of the coating "as supplied"

$(W_V)_a$	the weight percent of total volatiles in the coating "as applied"
$(W_V)_s$	the weight percent of total volatiles in the coating "as supplied"
$(W_W)_a$	the weight percent water in the coating "as applied"
$(W_W)_d$	the weight percent water in the dilution solvent
$(W_W)_s$	the weight percent water in the coating "as supplied"

1. INTRODUCTION

This Manual provides step-by-step instruction for preparation of two data sheets developed by the Environmental Protection Agency which may be used by coating manufacturers and users to present information on the quantity of volatile organic compounds* (VOC) emitted from a coating. One of the data sheets may be prepared by the manufacturer of the coating; the second would be used by the company that applies the coating to a substrate.

The first VOC data sheet, which would be prepared by the manufacturer, provides information on the volatile organic content of a coating as it is delivered to a customer. This is referred to as the VOC content of the coating "as supplied" (by the manufacturer to the user).

The second VOC data sheet, which would be prepared by the user or coater, provides information on the quantity of volatile organic compounds present as the coating is used or applied to the substrate and includes the effect of any dilution solvent added before application. This is referred to as the VOC content of the coating "as applied" (to the substrate).

The coating user may submit, and the Agency enforcing a regulation may accept, these data sheets as prima facie evidence of the actual VOC content of a coating. The referee method for ultimate determination of compliance, however, will continue to be the method specified in the applicable regulation (for example, EPA Reference Method 24 or individual ASTM methods).

*Volatile Organic Compound (VOC) - Any organic compound which participates in atmospheric photochemical reactions; that is, any organic compound other than those which the Administrator designates as having negligible photochemical reactivity. VOC may be measured by a reference method, an equivalent method, an alternative method, or by procedures specified under any regulation.

2. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS SUPPLIED" BY THE COATING MANUFACTURER TO THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS SUPPLIED" BY THE MANUFACTURER

Coating Manufacturer: _____

Coating Identification: _____

Batch Identification: _____

Supplied To: _____

Properties of the coating as supplied[1] to the customer:

A. Coating Density $(D_C)_S$: _____ lb/gal _____ kg/l

☐ ASTM D1475 ☐ Other[2]

B. Total Volatiles $(W_V)_S$: _____ Weight Percent

☐ ASTM D2369 ☐ Other[2]

C. Water Content: 1. $(W_W)_S$ _____ Weight Percent

☐ ASTM D3792 ☐ ASTM D4017 ☐ Other[2]

2. $(V_W)_S$ _____ Volume Percent

☐ Calculated ☐ Other[2]

D. Organic Volatiles $(W_O)_S$: _____ Weight Percent

E. Nonvolatiles Content $(V_n)_S$: _____ Volume Percent

F. VOC Content $(VOC)_S$: 1. _____ lb/gal coating less water

or _____ kg/l coating less water

2. _____ lb/gal solids

or _____ kg/l solids

Remarks: (use reverse side)

_____

[1]The subscript "s" denotes each value is for the coating "as supplied" by the manufacturer.

[2]Explain the other method used under "Remarks".

Signed: _____ Date _____

2.2 IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS SUPPLIED" COATINGS

This DATA SHEET is normally completed by the coating manufacturer and provided to the user.[1] It will henceforth be referred to as the "AS SUPPLIED" VOC DATA SHEET.

A. The "as supplied" coating density, $(D_c)_s$[2], is determined using "ASTM D1475 - Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in a coating, $(W_v)_s$, is determined by "ASTM D2369 - 81 Standard Method for Volatile Content of Coatings." drying conditions to be used are 110°C for 1 hour[3].

C. Water Content

1. The weight percent water, $(W_w)_s$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method."[3,4] An acceptable alternative to these procedures for purposes of preparing the data sheet would be to calculate the weight percent water from the manufacturer's coating formulation.

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[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "s" denotes those parameters of a coating when measured in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes a specified method does not give results that are representative of the actual cure mechanism, he may petition the enforcement authority for approval of an alternate analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and Federal enforcement agency.

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation should be treated in the same manner as water. The weight percent of negligibly reactive compounds in a coating should be determined from the manufacturer's formulation. The volume percent can then be calculated using equation II-1 when the weight percent and density of the negligibly reactive compounds are substituted for those of water. The weight and volume percent can be used in Equations II-2 and II-6, respectively, in place of $(W_w)_s$ and $(V_w)_s$.

2. The water content, in volume percent, $(V_w)_s$, can be calculated by the equation:

$$(V_w)_s = \frac{(W_w)_s (D_c)_s}{D_w}, \qquad \text{II-1}$$

where D_w is the density of water, 8.33 lbs/gal.

D. The organic volatiles content, $(W_o)_s$, i.e., the VOC content expressed as a percent by weight, is determined by the following equation[5]:

$$(W_o)_s = (W_v)_s - (W_w)_s \qquad \text{II-2}$$

If the coating contains no water the weight percent of organic volatiles is equal to the weight percent of total volatiles.

In other words:

$$(W_w)_s = 0 \text{ and}$$

$$(W_o)_s = (W_v)_s \qquad \text{II-3}$$

E. The volume percent solids (nonvolatiles), $(V_n)_s$, should be derived from the coating formulation using the following equation:

$$(V_n)_s = \sum_{i=1}^{p} (V_n)_{s_i} \qquad \text{II-4}$$

where $(V_n)_{s_i}$ denotes the volume percent of each nonvolatile component in an "as supplied" coating, and "p" is the number of nonvolatile components in that coating. (Also see Footnote 1, Pg. II-3.)

---

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean W_w and W_v values may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS SUPPLIED" VOC DATA SHEET.

F. The VOC content of the "as supplied" coating $(VOC)_s$ can now be calculated and thereby expressed in terms used by most State or Federal regulations.

1. The mass of VOC per unit volume of coating less water:

   a. If the coating contains no water, the equation is calculated as follows:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{100\%} \qquad \text{II-5}$$

   b. If the coating contains water, Equation II-5 becomes:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{100\% - (V_w)_s} \qquad \text{II-6}$$

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles). For both solvent-borne and waterborne coatings, the equation is:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{(V_n)_s} \qquad \text{II-7}$$

3. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS APPLIED" TO THE SUBSTRATE BY THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS APPLIED" TO THE SUBSTRATE

Coating Manufacturer: _____

Coating Identification: _____

Batch Identification: _____

User: _____

User's Coating Identification: _____

Properties of the coating as applied[1] by the User:

A. Coating Density $(D_c)_a$: _____ kg/l, or _____ lb/gal

☐ ASTM D1475 ☐ Other[2]

B. Total Volatiles $(W_v)_a$: _____ Weight Percent

☐ ASTM D2369 ☐ Other[2]

C. Water Content: 1. $(W_w)_a$ _____ Weight Percent

☐ ASTM D3792 ☐ ASTM D4017 ☐ Other[2]

2. $(V_w)_a$ _____ Volume Percent

☐ Calculated ☐ Other[2]

D. Weighted Average Density of the dilution solvent $(D_d)^3$: _____ lb/gal

☐ ASTM D1475 ☐ Handbook ☐ Formulation

(Continued on Reverse Side)

[1]The subscript "a" denotes each value is for the coating "as applied" to the substrate.
[2]Explain the other method used under "Remarks" on reverse side
[3]The subscript "d" denotes values are for the dilution solvent

E. Dilution Solvent Ratio (R_d): _____ $\frac{\text{gal diluent}}{(\text{gal coating})_s}$[4]

or

_____ $\frac{\text{liter diluent}}{(\text{liter coating})_s}$[4]

F. Organic Volatiles Content[5] $(W_o)_a$: _____ Weight Percent

G. Non-Volatiles Content $(V_n)_a$: _____ Volume Percent

H. VOC Content $(VOC)_a$: 1. _____ lb/gal of coating less water

or_____ kg/l of coating less water

2. _____ lb/gal solids

or_____ kg/l solids

REMARKS:

Signed: _____ Date: _____

---

[4]The subscript "s" denotes values are for the coating "as supplied" by the manufacturer.

[5]This terminology is used to be consistent with Method 24. It refers to all photochemically reactive organic compounds emitted from the coating including reactive by-products of the cure reaction, exactly the same matter as indicated in Paragraph H, i.e., volatile organic compounds, or VOC.

3.2. IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS APPLIED" COATINGS

This DATA SHEET, henceforth referred to as the "AS APPLIED" VOC DATA SHEET, is to be completed by the company which applies a coating. It provides information on the amount of volatile organic compounds (VOC) in the coating "as applied" to the substrate by accounting for the quantity of diluent solvent added to the "as supplied" coating prior to application. If a coating is diluted only with water or a solvent of negligible photochemical reactivity, the user merely doucments the fact (see Step E.1. and also Footnote 4, Pg. III-5.). Otherwise, several avenues exist for the coater to certify the VOC content:
(1) Maintain adequate records of how much organic solvent is added to each coating and use that information and the "AS SUPPLIED" VOC DATA SHEET[2] to calculate the VOC content "as applied." In this case begin with Step D.
(2) If the "AS SUPPLIED" DATA SHEET is available, but dilution records are not, begin the "As Applied" determination with Step A, skip Steps B and C, and proceed to Step D.
(The user may choose to analyze an "As Supplied" coating using Reference Method 24 and complete the "AS SUPPLIED" VOC DATA SHEET rather than have the coating manufacturer complete it. The volume percent solids, however, will necessarily continue to be supplied by the coating manufacturer.)
(3) Analyze each diluted coating with the same method used to generate the data provided by the coating manufacturer on the "AS SUPPLIED" VOC DATA SHEET. (See Chapter 2 of this Manual.) In this case begin with Step A.[1]

A. The "as applied" coating density, $(D_c)_a$[2], is determined using "ASTM D1475-Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in the coating, $(W_v)_a$ is determined by "ASTM D2369-81 Standard Method for Volatile Content of Coatings." The drying conditions to be used are 110°C for 1 hour[3].

---

[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "a" denotes those parameters of a coating in the "as applied" condition, i.e., after dilution by the user. The subscript "s" denotes the parameters of a coating in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes the specified method gives results that are not representative of the VOC released during the normal cure, he may petition the enforcement authority for approval of an alternative analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and/or Federal enforcement agency.

C. The water content is necessary only if the coating has been diluted with a mixture of organic solvent and water.[4,5] If the dilution solvent is 100 percent organic, or if the weight and volume percent water in the mixture is known, proceed directly to Step D.

The weight percent water, $(W_w)_a$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method." (Also see Footnote 3, Pg. III-4.)

The water content, in volume percent, $(V_w)_a$, can be calculated by the equation:

$$(V_w)_a = \frac{(W_w)_a \ (D_c)_a}{D_w} \qquad \text{III-1}$$

where D_w is the density of water, 8.33 lb/gal.

---

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation, should be treated in the same manner as water. The weight percent of negligibly reactive compounds in the dilution solvent must be known either from the coater's mixing records or the dilution solvent supplier's formulation. The volume percent can then be calculated using Equations III-1 or III-5 when the weight percent and density of the negligibly reactive organics are substituted for those of water. The weight and volume percent of the negligibly reactive compounds can be substituted in all equations where the weight and volume percent water, (W_w) and (V_w), respectively, are used.

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean weight percent water and total volatiles, W_w and W_v respectively, may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS APPLIED" VOC DATA SHEET.

D. If the dilution solvent consists of a single compound the density may be obtained from the literature.

If the dilution solvent is a mixture of organic compounds, the density, D_d[6], can be determined analytically via ASTM D1475, or an average density can be estimated from the solvent formulation as shown below. This estimation assumes that volumes are additive.

$$D_d = \frac{100\%}{\sum_{j=1}^{m} \frac{W_j}{D_j}} \qquad \text{III-2}$$

or

$$= \frac{1}{100\%} \sum_{j=1}^{m} V_j D_j \qquad \text{III-3}$$

where: D_j, W_j, and V_j denote the density, weight percent, and volume percent of each solvent in the dilution solvent mixture and "m" is the number of organic solvents in the dilution solvent mixture.

If the dilution solvent is a mixture of photochemically reactive organics and water, the coater must know the weight percent, $(W_w)_d$, or volume percent, $(V_w)_d$, of water from his mixing records or the supplier's formulation, or he must analytically determine the weight fraction of water in the dilution solvent using ASTM D3792 or ASTM D4017. The density, D_d, of the dilution solvent may then be determined by analytically measuring the density of the organic solvent/water mixture, $D_d^{\dagger}$, using ASTM D1475 and adjusting it for the water content using the following equation. (See also Footnote 4, Pg. III-5.)

$$D_d = D_d^{\dagger} \frac{[100\% - (W_w)_d]}{[100\% - (V_w)_d]} \qquad \text{III-4}$$

Note: If either the weight or volume percent water in the dilution solvent is known, the other can be calculated by the equation:

$$(V_w)_d = \frac{(W_w)_d \; D_d^{\dagger}}{D_w} \qquad \text{III-5}$$

where "D_w" is the density of water.

---

[6]The subscript "d" denotes a parameter that pertains to that solvent used by the coater to dilute the "as supplied" coating.

E. The dilution solvent ratio, R_d, is defined as the volume of photochemically reactive organic solvent, (VOC), added per unit volume of "as supplied" coating. Stated mathematically,

$$R_d = \frac{\text{Volume photochemically reactive dilution solvent added}}{\text{Volume of "as supplied" coating}}$$

1. If the "as supplied" coating is subsequently diluted with water or a solvent which is of negligible photochemical reactivity, the VOC content will be unchanged from that reported on the "AS SUPPLIED" VOC DATA SHEET. This should be reported on the "AS APPLIED" VOC DATA SHEET by entering "0" for the dilution solvent ratio, R_d.

2. In the absence of adequate dilution records, R_d can be calculated from entries on the VOC DATA SHEETS by one of the following equations:

   a. When the dilution solvent consists only of VOC,

$$R_d = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)} \qquad \text{III-6}$$

   b. When the dilution solvent is a mixture of water and photochemically reactive organic solvent, Equation III-6 may be expressed as:

$$R_d^{\dagger} = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)^{\dagger}} \qquad \text{III-7}$$

   where: $R_d^{\dagger}$ is the ratio of the volume of water and organic dilution solvent to the volume of "as supplied" coating to which it is added. (Also see Footnote 4, Pg. III-5.)

The dilution solvent ratio, R_d, may now be calculated from $R_d^{\dagger}$ by the following equation:

$$R_d = R_d^{\dagger} \left[1 - \frac{(V_w)_d}{100\%}\right] \qquad \text{III-8}$$

F. The organic volatile content $(W_o)_a$, i.e. the VOC content expressed as a percent by weight of the diluted coating, can now be calculated by either of two ways:

1. From analyses of the coating using the following equation:

$$(W_o)_a = (W_v)_a - (W_w)_a \qquad \text{III-9}$$

(See Footnotes 4 and 5, Pg. III-5.)

If the coating does not contain water, the weight percent of organic volatiles is equal to the weight percent of total volatiles, or

$$(W_o)_a = (W_v)_a \qquad \text{III-}$$

2. By using the data from the "AS SUPPLIED" VOC DATA SHEET, the dilution solvent ratio, and the density of the dilution solvent with the following equation:

$$(W_o)_a = \frac{[(D_c)_s\ (W_o)_s/100\%] + (R_d D_d)}{(D_c)_s + (R_d D_d)} \times 100\% \qquad \text{III-}$$

G. The volume percent solids, or nonvolatiles, $(V_n)_a$, must be calculated from the following equation where $(V_n)_s$ is obtained from the "AS SUPPLIED" VOC DATA SHEET.

$$(V_n)_a = \frac{(V_n)_s}{1 + R_d} \qquad \text{III-}$$

H. The VOC content of the "as applied" coating $(VOC)_a$, can now be calculated and thereby expressed in terms used in most State or Federa regulations.

1. The mass of VOC per unit volume of coating, less water, is calculated in either of two ways.

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM Methods:

(1). If the coating contains no water the equation is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\%} \qquad \text{III-}$$

(2). If the coating contains water the following equation must be used:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\% - (V_w)_a} \qquad \text{III-14}$$

b. Using the VOC content of the "as supplied" coating, (VOC_s), the dilution solvent ratio, and the density of the solvent, the equation is:

$$(VOC)_a = \frac{[(VOC)_s\ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{1 + R_d - (V_w)_s/100\%} \qquad \text{III-15}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles).

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM methods, the equation for both solvent-borne and waterborne coatings, is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{(V_n)_a} \qquad \text{III-16}$$

b. Using dilution information and calculation procedures only, the equation is:

$$(VOC)_a = \frac{[(VOC)_s\ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{(V_n)_s/100\%} \qquad \text{III-17}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA 450/3-84-019	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings	5. REPORT DATE December 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Air Quality Planning and Standards U. S. Environmental Protection Agency (MD-13) Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
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	14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This manual provides procedures by which firms may voluntarily certify the quantity of volatile organic compounds which will be emitted by a paint, ink, or other coating. Two data sheets are provided. One is to be used by the manufacturer of the coating, the other by the user. Analytical test methods and procedures for preparing the data sheets are included, as are the equations and instructions necessary to convert the analytical results into a format suitable for determining compliance with State or Federal regulations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Coatings Compliance Calculations Pollution Control Reference Method 24 Test Methods Volatile Organic Compounds	Air Pollution Control	13-B

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APPENDIX C

REFERENCE METHOD 24

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475–60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference—see § 60.17).

2.2 ASTM D2369–81, Standard Test Method for Volatile Content of Coatings (incorporated by reference—see § 60.17).

2.3 ASTM D3792–79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference—see § 60.17).

2.4 ASTM D4017–81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference—see § 60.17).

3. *Procedure.*

3.1 Volatile Matter Content. Use the procedure in ASTM D2369–81 (incorporated by reference—see § 60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1—Weight of dish and sample before heating, g.

W_2—Weight of dish and sample after heating, g.

W_3—Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{(Eq. 24-1)}$$

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water ($_w$) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference—see § 60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D1475–60 (Reapproved 1980) (incorporated by reference—see § 60.17).

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v
Water content, W_w	2.9 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter.

4.3 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures

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4. TITLE AND SUBTITLE A Guideline for Surface Coating Calculations	5. REPORT DATE February 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) PEI Associates, Inc.	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS PEI Associates, Inc. 1006 North Bowen Road Suite 201 Arlington, Texas 76012	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-3963
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16. ABSTRACT

The calculation of volatile organic compound emissions from surface coating operations to determine compliance is often a complicated task, sometimes creating confusion with compliance authorities and sources alike. In an attempt to minimize this confusion, EPA (OAQPS) has periodically issued guidance in this area, generally in the form of memoranda to the EPA Regional Offices. The most recent document is entitled "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings," published December 1984, EPA 450/3-84-019.

"A Guideline for Surface Coating Calculations" takes the above guidance process one step further for surface coating operations. Guidance is provided on how to compute existing and allowed emissions based on the above document as well as previously issued Control Technique Guidelines for the individual categories. Example calculations are included for basic emission problems, compliance determinations, equivalency determinations, application of transfer efficiency, and calculations involving complex multiproduct plants. The appropriate data sheets, a list of various equations and notations, and graphs and tables useful in making the above calculations are also included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Surface Coating VOC Data Sheets Calculations Compliance Determination Control Strategy Evaluation	Air Pollution Control Organic Chemicals Coating Operations	

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Research Triangle Park NC 27711

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December 1984

Air

EPA

Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings

NOTICE

THIS EDITION INCLUDES PAGES III-4
AND III-9 AS REVISED JUNE 19,1986

EPA-450/3-84-019

Procedure for Certifying Quantity of Volatile Organic Compounds Emitted By Paint, Ink, and Other Coatings

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1984

This report has been reviewed by the Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Copies of this report are available through the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711, or from the National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

PREFACE

This manual was conceived as a way to provide simple step-by-step instructions for certifying the quantity of volatile organic compounds (VOC) that will be released by a coating. It has not turned out that way. The guidance is here, but in spite of great diligence, the instructions remain imposing.

The manual was prepared for several reasons. First, the coatings industry, as represented by the National Paint and Coatings Association, had requested a certification procedure which would relieve their customers the expense of analysis. Second, the complexity of the calculations necessary to determine compliance, for example, when dilution solvent is added to a coating, continue to confound Federal, State and Local enforcement personnel. Finally, results of a recent review of the Agency's reference method for determining VOC reemphasized the importance of analytical procedures to verify VOC content.

In response to the results of the review of the test methods, this manual reaffirms that Reference Method 24 or its constituent methods developed by the American Society for Testing and Materials (ASTM), are the procedures by which the VOC content of a coating will be determined for compliance with Federal regulations. The earliest guidance was not so specific. In 1977, the first report[1], written to assist States in developing regulations for sources of VOC emissions, provided recommendations for the maximum allowable VOC content for complying coatings in a variety of industries. These values were expressed in mass of VOC per unit volume of coating. In deriving the recommended limitation, the VOC content of a coating was calculated based on the solids content provided by the coating manufacturer. The Agency calculated the mass of VOC in the coating by assuming the VOC had a density of 7.36 pounds per gallon.

Solvent and VOC were used somewhat interchangebly even though it was recognized that organics such as resin monomer, oligimers, and reaction by-products could be released by a coating during the cure. There was no accepted analytical method available for measuring the total VOC which would be released by a coating. The initial guidance[1] provided an analytical method for use only for air-dry coatings, those where all VOC emissions would be expected to come as a result of evaporation of solvent. On a volume basis, air dry coatings constituted the largest catagory of coatings then in use.

The Agency subsequently developed a more general analytical procedure that could be used to determine the total VOC in a coating. On October 3, 1980, the Agency published "Reference Method 24 (RM-24) -

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[1]Control of Volatile Organic Emissions from Stationary Sources - Volume II: Surface Caoting of Cans, Coils, Paper Fabrics, Automobiles, and Light-duty Trucks, Document No. EPA-450/2-77-008

Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings," in the Federal Register (45 FR 65958). For the first time the Agency formally specified an analytical method for the VOC content of those coatings that cure by chemical reaction. Even then, the announcement continued to allow the manufacturer's formulation to be used to calculate the VOC content but specified that the analytical technique, RM-24, would be the reference in any conflict between the two.

During 1981 and 1982, as more State and Federal regulations were established, the demand for low-solvent coatings began a continuing increase in the sales volume of reaction-cure coatings. There was some concern voiced by the industry in how appropriate the reference method was for these type coatings. To find out, the Agency began a review of RM-24 to determine the effect of temperature and exposure time on the indicated VOC "content". It was concluded that the maximum effect of those time-temperature combinations that were examined amounted to only about a 10 percent variation. Somewhat more surprising was that the solvent sometimes accounted for only 50 to 70 percent of the total VOC measured by the reference method.

The obvious conclusion was that RM-24 is a better measure of the total organics freed by a coating than is the solvent. This manual implements a policy based on that conclusion. Certification of VOC content on the attached Data Sheets must be based on an analysis using RM-24. No longer will solvent content be permitted as a surrogate for VOC unless a showing is first made that its use is a reasonable alternative or equivalent method of determining the VOC content of that particular coating.

One final comment. Since VOC is not always synonomous with solvent, it follows that the amount of solids in a coating cannot be obtained by subtracting the solvent from the total volume of coating. The original Federal Register proposal for RM-24, published on October 3, 1980, recommended the American Society of Test Materials test Number D2697 as the appropriate method of determining solids content. Subsequent comments from the industry maintained that this test is unreliable. As a result, when promulgated in 1980, RM-24 specified that the solids content of a coating can be obtained only from the manufacturer's formulation of the coating.

Dennis Crumpler

Dennis Crumpler
December 14, 1984

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GLOSSARY OF TERMS

"As Applied"	the condition of a coating after dilution by the user just prior to application to the substrate.
"As Supplied"	the condition of a coating before dilution, as sold and delivered by the coating manufacturer to the user.
$(D_c)_a$	coating density "as applied"
$(D_c)_s$	coating density, "as supplied"
D_d	density of dilution solvent
$D_d^{\dagger}$	density of organic solvent/water mixture
D_w	density of water (8.33 lb/gal)
R_d	dilution solvent ratio, equals the volume of VOC added per unit volume of coating "as supplied"
$R_d^{\dagger}$	equals the volume of premixed water and VOC added per unit volume of coating "as supplied"
$(V_n)_a$	Volume percent solids of coating "as applied"
$(V_n)_s$	Volume percent solids of coating "as supplied"
$(VOC)_a$	VOC content of "as applied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(VOC)_s$	VOC content of "as supplied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(V_w)_a$	the water content, in volume percent, of coating "as applied"
$(V_w)_d$	the water content, in volume percent, of the dilution solvent added to the "as supplied" coating
$(V_w)_s$	the water content, in volume percent, of the coating "as supplied"
$(W_o)_a$	the organic volatile content, in weight percent, of the coating "as applied"
$(W_o)_s$	the organic volatile content, in weight percent, of the coating "as supplied"

$(W_v)_a$	the weight percent of total volatiles in the coating "as applied"
$(W_v)_s$	the weight percent of total volatiles in the coating "as supplied"
$(W_w)_a$	the weight percent water in the coating "as applied"
$(W_w)_d$	the weight percent water in the dilution solvent
$(W_w)_s$	the weight percent water in the coating "as supplied"

1. INTRODUCTION

This Manual provides step-by-step instruction for preparation of two data sheets developed by the Environmental Protection Agency which may be used by coating manufacturers and users to present information on the quantity of volatile organic compounds* (VOC) emitted from a coating. One of the data sheets may be prepared by the manufacturer of the coating; the second would be used by the company that applies the coating to a substrate.

The first VOC data sheet, which would be prepared by the manufacturer, provides information on the volatile organic content of a coating as it is delivered to a customer. This is referred to as the VOC content of the coating "as supplied" (by the manufacturer to the user).

The second VOC data sheet, which would be prepared by the user or coater, provides information on the quantity of volatile organic compounds present as the coating is used or applied to the substrate and includes the effect of any dilution solvent added before application. This is referred to as the VOC content of the coating "as applied" (to the substrate).

The coating user may submit, and the Agency enforcing a regulation may accept, these data sheets as prima facie evidence of the actual VOC content of a coating. The referee method for ultimate determination of compliance, however, will continue to be the method specified in the applicable regulation (for example, EPA Reference Method 24 or individual ASTM methods).

*Volatile Organic Compound (VOC) - Any organic compound which participates in atmospheric photochemical reactions; that is, any organic compound other than those which the Administrator designates as having negligible photochemical reactivity. VOC may be measured by a reference method, an equivalent method, an alternative method, or by procedures specified under any regulation.

2. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS SUPPLIED" BY THE COATING MANUFACTURER TO THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS SUPPLIED" BY THE MANUFACTURER

Coating Manufacturer: _____

Coating Identification: _____

Batch Identification: _____

Supplied To: _____

Properties of the coating as supplied[1] to the customer:

A. Coating Density $(D_c)_s$: _____ lb/gal _____ kg/l .

☐ ASTM D1475 ☐ Other[2]

B. Total Volatiles $(W_v)_s$: _____ Weight Percent

☐ ASTM D2369 ☐ Other[2]

C. Water Content: 1. $(W_w)_s$ _____ Weight Percent

☐ ASTM D3792 ☐ ASTM D4017 ☐ Other[2]

2. $(V_w)_s$ _____ Volume Percent

☐ Calculated ☐ Other[2]

D. Organic Volatiles $(W_o)_s$: _____ Weight Percent

E. Nonvolatiles Content $(V_n)_s$: _____ Volume Percent

F. VOC Content $(VOC)_s$: 1. _____ lb/gal coating less water

or _____ kg/l coating less water

2. _____ lb/gal solids

or _____ kg/l solids

Remarks: (use reverse side)

_____

[1]The subscript "s" denotes each value is for the coating "as supplied" by the manufacturer.

[2]Explain the other method used under "Remarks".

Signed: _____ Date _____

2.2 IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS SUPPLIED" COATINGS

This DATA SHEET is normally completed by the coating manufacturer and provided to the user.[1] It will henceforth be referred to as the "AS SUPPLIED" VOC DATA SHEET.

A. The "as supplied" coating density, $(D_c)_s$[2], is determined using "ASTM D1475 - Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in a coating, $(W_v)_s$, is determined by "ASTM D2369 - 81 Standard Method for Volatile Content of Coatings." drying conditions to be used are 110°C for 1 hour[3].

C. Water Content

1. The weight percent water, $(W_w)_s$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method."[3,4] An acceptable alternative to these procedures for purposes of preparing the data sheet would be to calculate the weight percent water from the manufacturer's coating formulation.

---

[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "s" denotes those parameters of a coating when measured in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes a specified method does not give results that are representative of the actual cure mechanism, he may petition the enforcement authority for approval of an alternate analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and Federal enforcement agency.

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation should be treated in the same manner as water. The weight percent of negligibly reactive compounds in a coating should be determined from the manufacturer's formulation. The volume percent can then be calculated using equation II-1 when the weight percent and density of the negligibly reactive compounds are substituted for those of water. The weight and volume percent can be used in Equations II-2 and II-6, respectively, in place of $(W_w)_s$ and $(V_w)_s$.

2. The water content, in volume percent, $(V_w)_s$, can be calculated by the equation:

$$(V_w)_s = \frac{(W_w)_s (D_c)_s}{D_w}, \qquad \text{II-1}$$

where D_w is the density of water, 8.33 lbs/gal.

D. The organic volatiles content, $(W_o)_s$, i.e., the VOC content expressed as a percent by weight, is determined by the following equation[5]:

$$(W_o)_s = (W_v)_s - (W_w)_s \qquad \text{II-2}$$

If the coating contains no water the weight percent of organic volatiles is equal to the weight percent of total volatiles.

In other words:

$$(W_w)_s = 0 \text{ and}$$

$$(W_o)_s = (W_v)_s \qquad \text{II-3}$$

E. The volume percent solids (nonvolatiles), $(V_n)_s$, should be derived from the coating formulation using the following equation:

$$(V_n)_s = \sum_{i=1}^{p} (V_n)_{s_i} \qquad \text{II-4}$$

where $(V_n)_{s_i}$ denotes the volume percent of each nonvolatile component in an "as supplied" coating, and "p" is the number of nonvolatile components in that coating. (Also see Footnote 1, Pg. II-3.)

---

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean W_w and W_v values may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS SUPPLIED" VOC DATA SHEET.

F. The VOC content of the "as supplied" coating $(VOC)_s$ can now be calculated and thereby expressed in terms used by most State or Federal regulations.

1. The mass of VOC per unit volume of coating less water:

   a. If the coating contains no water, the equation is calculated as follows:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{100\%} \qquad \text{II-5}$$

   b. If the coating contains water, Equation II-5 becomes:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{100\% - (V_w)_s} \qquad \text{II-6}$$

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles). For both solvent-borne and waterborne coatings, the equation is:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{(V_n)_s} \qquad \text{II-7}$$

3. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS APPLIED" TO THE SUBSTRATE BY THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS APPLIED" TO THE SUBSTRATE

Coating Manufacturer: _____

Coating Identification: _____

Batch Identification: _____

User: _____

User's Coating Identification: _____

Properties of the coating as applied[1] by the User:

A. Coating Density $(D_c)_a$: _____ kg/l, or _____ lb/gal

☐ ASTM D1475 ☐ Other[2]

B. Total Volatiles $(W_v)_a$: _____ Weight Percent

☐ ASTM D2369 ☐ Other[2]

C. Water Content: 1. $(W_w)_a$ _____ Weight Percent

☐ ASTM D3792 ☐ ASTM D4017 ☐ Other[2]

2. $(V_w)_a$ _____ Volume Percent

☐ Calculated ☐ Other[2]

D. Weighted Average Density of the dilution solvent $(D_d)^3$: _____ lb/gal

☐ ASTM D1475 ☐ Handbook ☐ Formulation

(Continued on Reverse Side)

[1]The subscript "a" denotes each value is for the coating "as applied" to the substrate.
[2]Explain the other method used under "Remarks" on reverse side
[3]The subscript "d" denotes values are for the dilution solvent

E. Dilution Solvent Ratio (R_d): _____ $\frac{\text{gal diluent}}{(\text{gal coating})_s}$[4]

or

_____ $\frac{\text{liter diluent}}{(\text{liter coating})_s}$[4]

F. Organic Volatiles Content[5] $(W_o)_a$: _____ Weight Percent

G. Non-Volatiles Content $(V_n)_a$: _____ Volume Percent

H. VOC Content $(VOC)_a$: 1. _____ lb/gal of coating less water

or_____ kg/l of coating less water

2. _____ lb/gal solids

or_____ kg/l solids

REMARKS:

Signed: _____ Date: _____

---

[4]The subscript "s" denotes values are for the coating "as supplied" by the manufacturer.

[5]This terminology is used to be consistent with Method 24. It refers to all photochemically reactive organic compounds emitted from the coating including reactive by-products of the cure reaction, exactly the same matter as indicated in Paragraph H, i.e., volatile organic compounds, or VOC.

3.2. IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS APPLIED" COATINGS

This DATA SHEET, henceforth referred to as the "AS APPLIED" VOC DATA SHEET, is to be completed by the company which applies a coating. It provides information on the amount of volatile organic compounds (VOC) in the coating "as applied" to the substrate by accounting for the quantity of diluent solvent added to the "as supplied" coating prior to application. If a coating is diluted only with water or a solvent of negligible photochemical reactivity, the user merely doucments the fact (see Step E.1. and also Footnote 4, Pg. III-5.). Otherwise, several avenues exist for the coater to certify the VOC content:

(1) Maintain adequate records of how much organic solvent is added to each coating and use that information and the "AS SUPPLIED" VOC DATA SHEET[2] to calculate the VOC content "as applied." In this case begin with Step D.

(2) If the "AS SUPPLIED" DATA SHEET is available, but dilution records are not, begin the "As Applied" determination with Step A, skip Steps B and C, and proceed to Step D.

(The user may choose to analyze an "As Supplied" coating using Reference Method 24 and complete the "AS SUPPLIED" VOC DATA SHEET rather than have the coating manufacturer complete it. The volume percent solids, however, will necessarily continue to be supplied by the coating manufacturer.)

(3) Analyze each diluted coating with the same method used to generate the data provided by the coating manufacturer on the "AS SUPPLIED" VOC DATA SHEET. (See Chapter 2 of this Manual.) In this case begin with Step A.[1]

A. The "as applied" coating density, $(D_c)_a$[2], is determined using "ASTM D1475-Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in the coating, $(W_v)_a$ is determined by "ASTM D2369-81 Standard Method for Volatile Content of Coatings." The drying conditions to be used are 110°C for 1 hour[3].

---

[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "a" denotes those parameters of a coating in the "as applied" condition, i.e., after dilution by the user. The subscript "s" denotes the parameters of a coating in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes the specified method gives results that are not representative of the VOC released during the normal cure, he may petition the enforcement authority for approval of an alternative analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and/or Federal enforcement agency.

C. The water content is necessary only if the coating has been diluted with a mixture of organic solvent and water.[4],[5] If the dilution solvent is 100 percent organic, or if the weight and volume percent water in the mixture is known, proceed directly to Step D.

The weight percent water, $(W_w)_a$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method." (Also see Footnote 3, Pg. III-4.)

The water content, in volume percent, $(V_w)_a$, can be calculated by the equation:

$$(V_w)_a = \frac{(W_w)_a \ (D_c)_a}{D_w} \qquad \text{III-1}$$

where D_w is the density of water, 8.33 lb/gal.

---

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation, should be treated in the same manner as water. The weight percent of negligibly reactive compounds in the dilution solvent must be known either from the coater's mixing records or the dilution solvent supplier's formulation. The volume percent can then be calculated using Equations III-1 or III-5 when the weight percent and density of the negligibly reactive organics are substituted for those of water. The weight and volume percent of the negligibly reactive compounds can be substituted in all equations where the weight and volume percent water, (W_w) and (V_w), respectively, are used.

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean weight percent water and total volatiles, W_w and W_v respectively, may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS APPLIED" VOC DATA SHEET.

D. If the dilution solvent consists of a single compound the density may be obtained from the literature.

If the dilution solvent is a mixture of organic compounds, the density, D_d[6], can be determined analytically via ASTM D1475, or an average density can be estimated from the solvent formulation as shown below. This estimation assumes that volumes are additive.

$$D_d = \frac{100\%}{\sum_{j=1}^{m} \frac{W_j}{D_j}} \qquad \text{III-2}$$

or

$$= \frac{1}{100\%} \sum_{j=1}^{m} V_j D_j \qquad \text{III-3}$$

where: D_j, W_j, and V_j denote the density, weight percent, and volume percent of each solvent in the dilution solvent mixture and "m" is the number of organic solvents in the dilution solvent mixture.

If the dilution solvent is a mixture of photochemically reactive organics and water, the coater must know the weight percent, $(W_w)_d$, or volume percent, $(V_w)_d$, of water from his mixing records or the supplier's formulation, or he must analytically determine the weight fraction of water in the dilution solvent using ASTM D3792 or ASTM D4017. The density, D_d, of the dilution solvent may then be determined by analytically measuring the density of the organic solvent/water mixture, $D_d^{\dagger}$, using ASTM D1475 and adjusting it for the water content using the following equation. (See also Footnote 4, Pg. III-5.)

$$D_d = D_d^{\dagger} \frac{[100\% - (W_w)_d]}{[100\% - (V_w)_d]} \qquad \text{III-4}$$

Note: If either the weight or volume percent water in the dilution solvent is known, the other can be calculated by the equation:

$$(V_w)_d = \frac{(W_w)_d \; D_d^{\dagger}}{D_w} \qquad \text{III-5}$$

where "D_w" is the density of water.

---

[6]The subscript "d" denotes a parameter that pertains to that solvent used by the coater to dilute the "as supplied" coating.

E. The dilution solvent ratio, R_d, is defined as the volume of photochemically reactive organic solvent, (VOC), added per unit volume of "as supplied" coating. Stated mathematically,

$$R_d = \frac{\text{Volume photochemically reactive dilution solvent added}}{\text{Volume of "as supplied" coating}}$$

1. If the "as supplied" coating is subsequently diluted with water or a solvent which is of negligible photochemical reactivity, the VOC content will be unchanged from that reported on the "AS SUPPLIED" VOC DATA SHEET. This should be reported on the "AS APPLIED" VOC DATA SHEET by entering "0" for the dilution solvent ratio, R_d.

2. In the absence of adequate dilution records, R_d can be calculated from entries on the VOC DATA SHEETS by one of the following equations:

   a. When the dilution solvent consists only of VOC,

$$R_d = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)} \qquad \text{III-6}$$

   b. When the dilution solvent is a mixture of water and photochemically reactive organic solvent, Equation III-6 may be expressed as:

$$R_d^{\dagger} = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)^{\dagger}} \qquad \text{III-7}$$

   where: $R_d^{\dagger}$ is the ratio of the volume of water and organic dilution solvent to the volume of "as supplied" coating to which it is added. (Also see Footnote 4, Pg. III-5.)

The dilution solvent ratio, R_d, may now be calculated from $R_d^{\dagger}$ by the following equation:

$$R_d = R_d^{\dagger} \left[1 - \frac{(V_w)_d}{100}\right] \qquad \text{III-8}$$

F. The organic volatile content $(W_o)_a$, i.e. the VOC content expressed as a percent by weight of the diluted coating, can now be calculated by either of two ways:

1. From analyses of the coating using the following equation:

$$(W_o)_a = (W_v)_a - (W_w)_a \qquad \text{III-}$$

(See Footnotes 4 and 5, Pg. III-5.)

If the coating does not contain water, the weight percent of organic volatiles is equal to the weight percent of total volatiles, or

$$(W_o)_a = (W_v)_a \qquad \text{III-}$$

2. By using the data from the "AS SUPPLIED" VOC DATA SHEET, the dilution solvent ratio, and the density of the dilution solvent with the following equation:

$$(W_o)_a = \frac{[(D_c)_s\ (W_o)_s/100\%] + (R_d D_d)}{(D_c)_s + (R_d D_d)} \times 100\% \qquad \text{III-}$$

G. The volume percent solids, or nonvolatiles, $(V_n)_a$, must be calculated from the following equation where $(V_n)_s$ is obtained from the "AS SUPPLIED" VOC DATA SHEET.

$$(V_n)_a = \frac{(V_n)_s}{1 + R_d} \qquad \text{III-}$$

H. The VOC content of the "as applied" coating $(VOC)_a$, can now be calculated and thereby expressed in terms used in most State or Federa regulations.

1. The mass of VOC per unit volume of coating, less water, is calculated in either of two ways.

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM Methods:

(1). If the coating contains no water the equation is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\%} \qquad \text{III-}$$

(2). If the coating contains water the following equation must be used:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\% - (V_w)_a} \qquad \text{III-14}$$

b. Using the VOC content of the "as supplied" coating, (VOC_s), the dilution solvent ratio, and the density of the solvent, the equation is:

$$(VOC)_a = \frac{[(VOC)_s\ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{1 + R_d - (V_w)_s/100\%} \qquad \text{III-15}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles).

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM methods, the equation for both solvent-borne and waterborne coatings, is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{(V_n)_a} \qquad \text{III-16}$$

b. Using dilution information and calculation procedures only, the equation is:

$$(VOC)_a = \frac{[(VOC)_s\ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{(V_n)_s/100\%} \qquad \text{III-17}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

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16. ABSTRACT

This manual provides procedures by which firms may voluntarily certify the quantity of volatile organic compounds which will be emitted by a paint, ink, or other coating. Two data sheets are provided. One is to be used by the manufacturer of the coating, the other by the user. Analytical test methods and procedures for preparing the data sheets are included, as are the equations and instructions necessary to convert the analytical results into a format suitable for determining compliance with State or Federal regulations.

17. KEY WORDS AND DOCUMENT ANALYSIS

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APPENDIX C

REFERENCE METHOD 24

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475–60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference—see § 60.17).

2.2 ASTM D2369–81, Standard Test Method for Volatile Content of Coatings (incorporated by reference—see § 60.17).

2.3 ASTM D3792–79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference—see § 60.17).

2.4 ASTM D4017–81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference—see § 60.17).

3. *Procedure.*

3.1 Volatile Matter Content. Use the procedure in ASTM D2369–81 (incorporated by reference—see § 60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_s = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_s} \qquad \text{(Eq. 24-1)}$$

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference—see § 60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D1475–60 (Reapproved 1980) (incorporated by reference—see § 60.17).

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v
Water content, W_w	2.8 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter.

4.3 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures

cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropirate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_v use the lower confidence limits, and for W_w use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-2}$$

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-4}$$

Where: W_s = Weight solids, g/g.

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PRINTING INKS AND RELATED COATINGS

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.

1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

2. *Procedure.*

2.1 Weight Fraction VOC.

2.1.1 Apparatus.

2.1.1.1 Weighing Dishes. Aluminum foil, 58 mm in diameter by 18 mm high, with a flat bottom. There must be at least three weighing dishes per sample.

2.1.1.2 Disposable syringe, 5 ml.

2.1.1.3 Analytical Balance. To measure to within 0.1 mg.

2.1.1.4 Oven. Vacuum oven capable of maintaining a temperature of 120±2°C and an absolute pressure of 510 ±51 mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2°C for 24 hours.

2.1.1.5 Analysis. Shake or mix the sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{wd}).

Using a 5-ml syringe without a needle remove a sample of the coating. Weigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{ss}). Transfer 1 to 3 g of the sample to the tared weighing dish. Reweigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{sf}). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of 510 ±51 mm Hg and a temperature of 120 ±2°C for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of 120 ±2°C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{wd}). Repeat this procedure for a total of three determinations for each sample.

2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D 1475-60 (Reapproved 1980), which is incorporated by reference. It is available from the American Society of Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. It is also available for inspection at the Office of the Federal Register, Room 8401, 1100 L Street, NW., Washington, D.C. This incorporation by reference was approved by the Director of the Federal Register on November 8, 1982. This material is incorporated as it exists on the date of approval and a notice of any change in these materials will be published in the FEDERAL REGISTER.

2.3 Solvent Density. Determine the density of the solvent according to the procedure outlined in ASTM D 1475-60 (reapproved 1980). Make a total of three determinations for each coating. Report the density D_v as the arithmetic average of the three determinations.

3. *Calculations.*

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content W_o using the following equation:

$$W_o = \frac{M_{s1} + M_{cv1} - M_{cv2} - M_{s2}}{M_{cv1} - M_{cv2}}$$

(Eq. 24A-1)

Report the weight fraction VOC $\overline{W}_o$ as the arithmetic average of the three determinations.

3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content V_o using the following equation:

$$W_o = \frac{M_{s1} + M_{cv1} - M_{cv2} - M_{s2}}{M_{cv1} - M_{cv2}}$$

Eq.24A-1

$$V_o + \frac{\overline{W}_o \overline{D}_c}{D_o}$$

Eq. 24A-2

4. *Bibliography.*

4.1 Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475-60 (Reapproved 1980).

4.2 Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R. A., Radian Corporation. September 25, 1979. Gravure Ink Analysis.

4.3 Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation. November 5, 1979. Gravure Ink Analysis.

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16. ABSTRACT

The calculation of volatile organic compound emissions from surface coating operations to determine compliance is often a complicated task, sometimes creating confusion with compliance authorities and sources alike. In an attempt to minimize this confusion, EPA (OAQPS) has periodically issued guidance in this area, generally in the form of memoranda to the EPA Regional Offices. The most recent document is entitled "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings," published December 1984, EPA 450/3-84-019.

"A Guideline for Surface Coating Calculations" takes the above guidance process one step further for surface coating operations. Guidance is provided on how to compute existing and allowed emissions based on the above document as well as previously issued Control Technique Guidelines for the individual categories. Example calculations are included for basic emission problems, compliance determinations, equivalency determinations, application of transfer efficiency, and calculations involving complex multiproduct plants. The appropriate data sheets, a list of various equations and notations, and graphs and tables useful in making the above calculations are also included.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Air

EPA

Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings

NOTICE

THIS EDITION INCLUDES PAGES III-4
AND III-9 AS REVISED JUNE 19,1986

EPA-450/3-84-019

Procedure for Certifying Quantity of Volatile Organic Compounds Emitted By Paint, Ink, and Other Coatings

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

December 1984

This report has been reviewed by the Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Copies of this report are available through the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711, or from the National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

PREFACE

This manual was conceived as a way to provide simple step-by-step instructions for certifying the quantity of volatile organic compounds (VOC) that will be released by a coating. It has not turned out that way. The guidance is here, but in spite of great diligence, the instructions remain imposing.

The manual was prepared for several reasons. First, the coatings industry, as represented by the National Paint and Coatings Association, had requested a certification procedure which would relieve their customers the expense of analysis. Second, the complexity of the calculations necessary to determine compliance, for example, when dilution solvent is added to a coating, continue to confound Federal, State and Local enforcement personnel. Finally, results of a recent review of the Agency's reference method for determining VOC reemphasized the importance of analytical procedures to verify VOC content.

In response to the results of the review of the test methods, this manual reaffirms that Reference Method 24 or its constituent methods developed by the American Society for Testing and Materials (ASTM), are the procedures by which the VOC content of a coating will be determined for compliance with Federal regulations. The earliest guidance was not so specific. In 1977, the first report[1], written to assist States in developing regulations for sources of VOC emissions, provided recommendations for the maximum allowable VOC content for complying coatings in a variety of industries. These values were expressed in mass of VOC per unit volume of coating. In deriving the recommended limitation, the VOC content of a coating was calculated based on the solids content provided by the coating manufacturer. The Agency calculated the mass of VOC in the coating by assuming the VOC had a density of 7.36 pounds per gallon.

Solvent and VOC were used somewhat interchangebly even though it was recognized that organics such as resin monomer, oligimers, and reaction by-products could be released by a coating during the cure. There was no accepted analytical method available for measuring the total VOC which would be released by a coating. The initial guidance[1] provided an analytical method for use only for air-dry coatings, those where all VOC emissions would be expected to come as a result of evaporation of solvent. On a volume basis, air dry coatings constituted the largest catagory of coatings then in use.

The Agency subsequently developed a more general analytical procedure that could be used to determine the total VOC in a coating. On October 3, 1980, the Agency published "Reference Method 24 (RM-24) -

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[1]Control of Volatile Organic Emissions from Stationary Sources - Volume II: Surface Caoting of Cans, Coils, Paper Fabrics, Automobiles, and Light-duty Trucks, Document No. EPA-450/2-77 [illegible]

Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings," in the Federal Register (45 FR 65958). For the first time the Agency formally specified an analytical method for the VOC content of those coatings that cure by chemical reaction. Even then, the announcement continued to allow the manufacturer's formulation to be used to calculate the VOC content but specified that the analytical technique, RM-24, would be the reference in any conflict between the two.

During 1981 and 1982, as more State and Federal regulations were established, the demand for low-solvent coatings began a continuing increase in the sales volume of reaction-cure coatings. There was some concern voiced by the industry in how appropriate the reference method was for these type coatings. To find out, the Agency began a review of RM-24 to determine the effect of temperature and exposure time on the indicated VOC "content". It was concluded that the maximum effect of those time-temperature combinations that were examined amounted to only about a 10 percent variation. Somewhat more surprising was that the solvent sometimes accounted for only 50 to 70 percent of the total VOC measured by the reference method.

The obvious conclusion was that RM-24 is a better measure of the total organics freed by a coating than is the solvent. This manual implements a policy based on that conclusion. Certification of VOC content on the attached Data Sheets must be based on an analysis using RM-24. No longer will solvent content be permitted as a surrogate for VOC unless a showing is first made that its use is a reasonable alternative or equivalent method of determining the VOC content of that particular coating.

One final comment. Since VOC is not always synonomous with solvent, it follows that the amount of solids in a coating cannot be obtained by subtracting the solvent from the total volume of coating. The original Federal Register proposal for RM-24, published on October 3, 1980, recommended the American Society of Test Materials test Number D2697 as the appropriate method of determining solids content. Subsequent comments from the industry maintained that this test is unreliable. As a result, when promulgated in 1980, RM-24 specified that the solids content of a coating can be obtained only from the manufacturer's formulation of the coating.

Dennis Crumpler

Dennis Crumpler
December 14, 1984

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GLOSSARY OF TERMS

"As Applied"	the condition of a coating after dilution by the user just prior to application to the substrate.
"As Supplied"	the condition of a coating before dilution, as sold and delivered by the coating manufacturer to the user.
$(D_c)_a$	coating density "as applied"
$(D_c)_s$	coating density, "as supplied"
D_d	density of dilution solvent
$D_d^{\dagger}$	density of organic solvent/water mixture
D_w	density of water (8.33 lb/gal)
R_d	dilution solvent ratio, equals the volume of VOC added per unit volume of coating "as supplied"
$R_d^{\dagger}$	equals the volume of premixed water and VOC added per unit volume of coating "as supplied"
$(V_n)_a$	Volume percent solids of coating "as applied"
$(V_n)_s$	Volume percent solids of coating "as supplied"
$(VOC)_a$	VOC content of "as applied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(VOC)_s$	VOC content of "as supplied" coating, expressed as mass of VOC per unit volume of coating less water or as mass of VOC per unit volume of solids
$(V_w)_a$	the water content, in volume percent, of coating "as applied"
$(V_w)_d$	the water content, in volume percent, of the dilution solvent added to the "as supplied" coating
$(V_w)_s$	the water content, in volume percent, of the coating "as supplied"
$(W_o)_a$	the organic volatile content, in weight percent, of the coating "as applied"
$(W_o)_s$	the organic volatile content, in weight percent, of the coating "as supplied"

$(W_v)_a$	the weight percent of total volatiles in the coating "as applied"
$(W_v)_s$	the weight percent of total volatiles in the coating "as supplied"
$(W_w)_a$	the weight percent water in the coating "as applied"
$(W_w)_d$	the weight percent water in the dilution solvent
$(W_w)_s$	the weight percent water in the coating "as supplied"

1. INTRODUCTION

This Manual provides step-by-step instruction for preparation of two data sheets developed by the Environmental Protection Agency which may be used by coating manufacturers and users to present information on the quantity of volatile organic compounds* (VOC) emitted from a coating. One of the data sheets may be prepared by the manufacturer of the coating; the second would be used by the company that applies the coating to a substrate.

The first VOC data sheet, which would be prepared by the manufacturer, provides information on the volatile organic content of a coating as it is delivered to a customer. This is referred to as the VOC content of the coating "as supplied" (by the manufacturer to the user).

The second VOC data sheet, which would be prepared by the user or coater, provides information on the quantity of volatile organic compounds present as the coating is used or applied to the substrate and includes the effect of any dilution solvent added before application. This is referred to as the VOC content of the coating "as applied" (to the substrate).

The coating user may submit, and the Agency enforcing a regulation may accept, these data sheets as prima facie evidence of the actual VOC content of a coating. The referee method for ultimate determination of compliance, however, will continue to be the method specified in the applicable regulation (for example, EPA Reference Method 24 or individual ASTM methods).

*Volatile Organic Compound (VOC) - Any organic compound which participates in atmospheric photochemical reactions; that is, any organic compound other than those which the Administrator designates as having negligible photochemical reactivity. VOC may be measured by a reference method, an equivalent method, an alternative method, or by procedures specified under any regulation.

2. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS SUPPLIED" BY THE COATING MANUFACTURER TO THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS SUPPLIED" BY THE MANUFACTURER

Coating Manufacturer: _____

Coating Identification: _____

Batch Identification: _____

Supplied To: _____

Properties of the coating as supplied[1] to the customer:

A. Coating Density $(D_C)_S$: _____ lb/gal _____ kg/l

☐ ASTM D1475 ☐ Other[2]

B. Total Volatiles $(W_V)_S$: _____ Weight Percent

☐ ASTM D2369 ☐ Other[2]

C. Water Content: 1. $(W_W)_S$ _____ Weight Percent

☐ ASTM D3792 ☐ ASTM D4017 ☐ Other[2]

2. $(V_W)_S$ _____ Volume Percent

☐ Calculated ☐ Other[2]

D. Organic Volatiles $(W_O)_S$: _____ Weight Percent

E. Nonvolatiles Content $(V_n)_S$: _____ Volume Percent

F. VOC Content $(VOC)_S$: 1. _____ lb/gal coating less water

or _____ kg/l coating less water

2. _____ lb/gal solids

or _____ kg/l solids

Remarks: (use reverse side)

_____

[1]The subscript "s" denotes each value is for the coating "as supplied" by the manufacturer.

[2]Explain the other method used under "Remarks".

Signed: _____ Date _____

2.2 IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS SUPPLIED" COATINGS

This DATA SHEET is normally completed by the coating manufacturer and provided to the user.[1] It will henceforth be referred to as the "AS SUPPLIED" VOC DATA SHEET.

A. The "as supplied" coating density, $(D_c)_s$[2], is determined using "ASTM D1475 - Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in a coating, $(W_v)_s$, is determined by "ASTM D2369 - 81 Standard Method for Volatile Content of Coatings." drying conditions to be used are 110°C for 1 hour[3].

C. Water Content

1. The weight percent water, $(W_w)_s$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method."[3,4] An acceptable alternative to these procedures for purposes of preparing the data sheet would be to calculate the weight percent water from the manufacturer's coating formulation.

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[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "s" denotes those parameters of a coating when measured in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes a specified method does not give results that are representative of the actual cure mechanism, he may petition the enforcement authority for approval of an alternate analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and Federal enforcement agency.

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation should be treated in the same manner as water. The weight percent of negligibly reactive compounds in a coating should be determined from the manufacturer's formulation. The volume percent can then be calculated using equation II-1 when the weight percent and density of the negligibly reactive compounds are substituted for those of water. The weight and volume percent can be used in Equations II-2 and II-6, respectively, in place of $(W_w)_s$ and $(V_w)_s$.

2. The water content, in volume percent, $(V_w)_s$, can be calculated by the equation:

$$(V_w)_s = \frac{(W_w)_s(D_c)_s}{D_w}, \qquad \text{II-1}$$

where D_w is the density of water, 8.33 lbs/gal.

D. The organic volatiles content, $(W_o)_s$, i.e., the VOC content expressed as a percent by weight, is determined by the following equation[5]:

$$(W_o)_s = (W_v)_s - (W_w)_s \qquad \text{II-2}$$

If the coating contains no water the weight percent of organic volatiles is equal to the weight percent of total volatiles.

In other words:

$$(W_w)_s = 0 \text{ and}$$

$$(W_o)_s = (W_v)_s \qquad \text{II-3}$$

E. The volume percent solids (nonvolatiles), $(V_n)_s$, should be derived from the coating formulation using the following equation:

$$(V_n)_s = \sum_{i=1}^{p} (V_n)_{s_i} \qquad \text{II-4}$$

where $(V_n)_{s_i}$ denotes the volume percent of each nonvolatile component in an "as supplied" coating, and "p" is the number of nonvolatile components in that coating. (Also see Footnote 1, Pg. II-3.)

---

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean W_w and W_v values may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS SUPPLIED" VOC DATA SHEET.

F. The VOC content of the "as supplied" coating $(VOC)_s$ can now be calculated and thereby expressed in terms used by most State or Federal regulations.

1. The mass of VOC per unit volume of coating less water:

   a. If the coating contains no water, the equation is calculated as follows:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{100\%} \qquad \text{II-5}$$

   b. If the coating contains water, Equation II-5 becomes:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{100\% - (V_w)_s} \qquad \text{II-6}$$

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles). For both solvent-borne and waterborne coatings, the equation is:

$$(VOC)_s = \frac{(W_o)_s\ (D_c)_s}{(V_n)_s} \qquad \text{II-7}$$

3. VOC CONTENT OF PAINT, INK AND OTHER COATINGS "AS APPLIED" TO THE SUBSTRATE BY THE USER

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

VOC DATA SHEET:

PROPERTIES OF THE COATING "AS APPLIED" TO THE SUBSTRATE

Coating Manufacturer: _____

Coating Identification: _____

Batch Identification: _____

User: _____

User's Coating Identification: _____

Properties of the coating as applied[1] by the User:

A. Coating Density $(D_c)_a$: _____ kg/l, or _____ lb/gal

☐ ASTM D1475 ☐ Other[2]

B. Total Volatiles $(W_v)_a$: _____ Weight Percent

☐ ASTM D2369 ☐ Other[2]

C. Water Content: 1. $(W_w)_a$ _____ Weight Percent

☐ ASTM D3792 ☐ ASTM D4017 ☐ Other[2]

2. $(V_w)_a$ _____ Volume Percent

☐ Calculated ☐ Other[2]

D. Weighted Average Density of the dilution solvent $(D_d)^3$: _____ lb/gal

☐ ASTM D1475 ☐ Handbook ☐ Formulation

(Continued on Reverse Side)

[1]The subscript "a" denotes each value is for the coating "as applied" to the substrate.
[2]Explain the other method used under "Remarks" on reverse side
[3]The subscript "d" denotes values are for the dilution solvent

E. Dilution Solvent Ratio (R_d): _____ $\frac{\text{gal diluent}}{(\text{gal coating})_s}$[4]

or

_____ $\frac{\text{liter diluent}}{(\text{liter coating})_s}$[4]

F. Organic Volatiles Content[5] $(W_o)_a$: _____ Weight Percent

G. Non-Volatiles Content $(V_n)_a$: _____ Volume Percent

H. VOC Content $(VOC)_a$: 1. _____ lb/gal of coating less water

or_____ kg/l of coating less water

2. _____ lb/gal solids

or_____ kg/l solids

REMARKS:

Signed: _____ Date: _____

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[4]The subscript "s" denotes values are for the coating "as supplied" by the manufacturer.

[5]This terminology is used to be consistent with Method 24. It refers to all photochemically reactive organic compounds emitted from the coating including reactive by-products of the cure reaction, exactly the same matter as indicated in Paragraph H, i.e., volatile organic compounds, or VOC.

3.2. IMPLEMENTING INSTRUCTIONS FOR THE VOC DATA SHEET FOR "AS APPLIED" COATINGS

This DATA SHEET, henceforth referred to as the "AS APPLIED" VOC DATA SHEET, is to be completed by the company which applies a coating. It provides information on the amount of volatile organic compounds (VOC) in the coating "as applied" to the substrate by accounting for the quantity of diluent solvent added to the "as supplied" coating prior to application. If a coating is diluted only with water or a solvent of negligible photochemical reactivity, the user merely doucments the fact (see Step E.1. and also Footnote 4, Pg. III-5.). Otherwise, several avenues exist for the coater to certify the VOC content:

(1) Maintain adequate records of how much organic solvent is added to each coating and use that information and the "AS SUPPLIED" VOC DATA SHEET[2] to calculate the VOC content "as applied." In this case begin with Step D.

(2) If the "AS SUPPLIED" DATA SHEET is available, but dilution records are not, begin the "As Applied" determination with Step A, skip Steps B and C, and proceed to Step D.
(The user may choose to analyze an "As Supplied" coating using Reference Method 24 and complete the "AS SUPPLIED" VOC DATA SHEET rather than have the coating manufacturer complete it. The volume percent solids, however, will necessarily continue to be supplied by the coating manufacturer.)

(3) Analyze each diluted coating with the same method used to generate the data provided by the coating manufacturer on the "AS SUPPLIED" VOC DATA SHEET. (See Chapter 2 of this Manual.) In this case begin with Step A.[1]

A. The "as applied" coating density, $(D_c)_a$[2], is determined using "ASTM D1475-Standard Test Method for Density of Paint, Lacquer, and Related Products."

B. The weight percent of total volatiles in the coating, $(W_v)_a$ is determined by "ASTM D2369-81 Standard Method for Volatile Content of Coatings." The drying conditions to be used are 110°C for 1 hour[3].

---

[1]EPA's Reference Method 24 (40 C.F.R. Part 60, App. A), contains the ASTM methods referenced in these instructions.

[2]The subscript "a" denotes those parameters of a coating in the "as applied" condition, i.e., after dilution by the user. The subscript "s" denotes the parameters of a coating in the "as supplied" condition, before dilution by the user.

[3]If the manufacturer believes the specified method gives results that are not representative of the VOC released during the normal cure, he may petition the enforcement authority for approval of an alternative analytical method. Any alternate method or alteration to the methods and procedures in these instructions or in any applicable regulation would be subject to review and approval by the appropriate State and/or Federal enforcement agency.

C. The water content is necessary only if the coating has been diluted with a mixture of organic solvent and water.[4,5] If the dilution solvent is 100 percent organic, or if the weight and volume percent water in the mixture is known, proceed directly to Step D.

The weight percent water, $(W_w)_a$, is determined by "ASTM D3792 - Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph," or "ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Method." (Also see Footnote 3, Pg. III-4.)

The water content, in volume percent, $(V_w)_a$, can be calculated by the equation:

$$(V_w)_a = \frac{(W_w)_a \ (D_c)_a}{D_w} \qquad \text{III-1}$$

where D_w is the density of water, 8.33 lb/gal.

---

[4]Volatile compounds classified by EPA as having negligible photochemical reactivity such as 1,1,1-trichloroethane and methylene chloride, etc., and listed as exempt in the applicable Federal and State VOC regulation, should be treated in the same manner as water. The weight percent of negligibly reactive compounds in the dilution solvent must be known either from the coater's mixing records or the dilution solvent supplier's formulation. The volume percent can then be calculated using Equations III-1 or III-5 when the weight percent and density of the negligibly reactive organics are substituted for those of water. The weight and volume percent of the negligibly reactive compounds can be substituted in all equations where the weight and volume percent water, (W_w) and (V_w), respectively, are used.

[5]The precision limit adjustments permitted by Reference Method 24 for experimentally determined mean weight percent water and total volatiles, W_w and W_v respectively, may be made only by enforcement agencies for determination of compliance. The adjustment is not to be used for the purposes of completing the "AS APPLIED" VOC DATA SHEET.

D. If the dilution solvent consists of a single compound the density may be obtained from the literature.

If the dilution solvent is a mixture of organic compounds, the density, D_d[6], can be determined analytically via ASTM D1475, or an average density can be estimated from the solvent formulation as shown below. This estimation assumes that volumes are additive.

$$D_d = \frac{100\%}{\sum_{j=1}^{m} \frac{W_j}{D_j}} \qquad \text{III-2}$$

or

$$= \frac{1}{100\%} \sum_{j=1}^{m} V_j D_j \qquad \text{III-3}$$

where: D_j, W_j, and V_j denote the density, weight percent, and volume percent of each solvent in the dilution solvent mixture and "m" is the number of organic solvents in the dilution solvent mixture.

If the dilution solvent is a mixture of photochemically reactive organics and water, the coater must know the weight percent, $(W_w)_d$, or volume percent, $(V_w)_d$, of water from his mixing records or the supplier's formulation, or he must analytically determine the weight fraction of water in the dilution solvent using ASTM D3792 or ASTM D4017. The density, D_d, of the dilution solvent may then be determined by analytically measuring the density of the organic solvent/water mixture, $D_d^{\dagger}$, using ASTM D1475 and adjusting it for the water content using the following equation. (See also Footnote 4, Pg. III-5.)

$$D_d = D_d^{\dagger} \frac{[100\% - (W_w)_d]}{[100\% - (V_w)_d]} \qquad \text{III-4}$$

Note: If either the weight or volume percent water in the dilution solvent is known, the other can be calculated by the equation:

$$(V_w)_d = \frac{(W_w)_d \; D_d^{\dagger}}{D_w} \qquad \text{III-5}$$

where "D_w" is the density of water.

---

[6]The subscript "d" denotes a parameter that pertains to that solvent used by the coater to dilute the "as supplied" coating.

E. The dilution solvent ratio, R_d, is defined as the volume of photochemically reactive organic solvent, (VOC), added per unit volume of "as supplied" coating. Stated mathematically,

$$R_d = \frac{\text{Volume photochemically reactive dilution solvent added}}{\text{Volume of "as supplied" coating}}$$

1. If the "as supplied" coating is subsequently diluted with water or a solvent which is of negligible photochemical reactivity, the VOC content will be unchanged from that reported on the "AS SUPPLIED" VOC DATA SHEET. This should be reported on the "AS APPLIED" VOC DATA SHEET by entering "0" for the dilution solvent ratio, R_d.

2. In the absence of adequate dilution records, R_d can be calculated from entries on the VOC DATA SHEETS by one of the following equations:

   a. When the dilution solvent consists only of VOC,

$$R_d = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)} \qquad \text{III-6}$$

   b. When the dilution solvent is a mixture of water and photochemically reactive organic solvent, Equation III-6 may be expressed as:

$$R_d^{\dagger} = \frac{(D_c)_s - (D_c)_a}{(D_c)_a - (D_d)^{\dagger}} \qquad \text{III-7}$$

   where: $R_d^{\dagger}$ is the ratio of the volume of water and organic dilution solvent to the volume of "as supplied" coating to which it is added. (Also see Footnote 4, Pg. III-5.)

The dilution solvent ratio, R_d, may now be calculated from $R_d^{\dagger}$ by the following equation:

$$R_d = R_d^{\dagger}\left[1 - \frac{(V_w)_d}{100\%}\right] \qquad \text{III-8}$$

F. The organic volatile content $(W_o)_a$, i.e. the VOC content expressed as a percent by weight of the diluted coating, can now be calculated by either of two ways:

1. From analyses of the coating using the following equation:

$$(W_o)_a = (W_v)_a - (W_w)_a \qquad \text{III-}$$

(See Footnotes 4 and 5, Pg. III-5.)

If the coating does not contain water, the weight percent of organic volatiles is equal to the weight percent of total volatiles, or

$$(W_o)_a = (W_v)_a \qquad \text{III-}$$

2. By using the data from the "AS SUPPLIED" VOC DATA SHEET, the dilution solvent ratio, and the density of the dilution solvent with the following equation:

$$(W_o)_a = \frac{[(D_c)_s\ (W_o)_s/100\%] + (R_d D_d)}{(D_c)_s + (R_d D_d)} \times 100\% \qquad \text{III-}$$

G. The volume percent solids, or nonvolatiles, $(V_n)_a$, must be calculated from the following equation where $(V_n)_s$ is obtained from the "AS SUPPLIED" VOC DATA SHEET.

$$(V_n)_a = \frac{(V_n)_s}{1 + R_d} \qquad \text{III-}$$

H. The VOC content of the "as applied" coating $(VOC)_a$, can now be calculated and thereby expressed in terms used in most State or Federa regulations.

1. The mass of VOC per unit volume of coating, less water, is calculated in either of two ways.

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM Methods:

(1). If the coating contains no water the equation is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\%} \qquad \text{III-}$$

(2). If the coating contains water the following equation must be used:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{100\% - (V_w)_a} \qquad \text{III-14}$$

b. Using the VOC content of the "as supplied" coating, (VOC_s), the dilution solvent ratio, and the density of the solvent, the equation is:

$$(VOC)_a = \frac{[(VOC)_s\ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{1 + R_d - (V_w)_s/100\%} \qquad \text{III-15}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

2. The VOC content may also be calculated in terms of mass of VOC per unit volume of solids (nonvolatiles).

a. Using the results obtained by analyzing the coating with EPA Reference Method 24 or its constituent ASTM methods, the equation for both solvent-borne and waterborne coatings, is:

$$(VOC)_a = \frac{(W_o)_a\ (D_c)_a}{(V_n)_a} \qquad \text{III-16}$$

b. Using dilution information and calculation procedures only, the equation is:

$$(VOC)_a = \frac{[(VOC)_s\ (100\% - (V_w)_s)/100\%] + (R_d D_d)}{(V_n)_s/100\%} \qquad \text{III-17}$$

Where $(VOC)_s$ in this case must be in units of lbs VOC/gal coating less water.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA 450/3-84-019	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink, and Other Coatings	5. REPORT DATE December 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Air Quality Planning and Standards U. S. Environmental Protection Agency (MD-13) Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This manual provides procedures by which firms may voluntarily certify the quantity of volatile organic compounds which will be emitted by a paint, ink, or other coating. Two data sheets are provided. One is to be used by the manufacturer of the coating, the other by the user. Analytical test methods and procedures for preparing the data sheets are included, as are the equations and instructions necessary to convert the analytical results into a format suitable for determining compliance with State or Federal regulations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN-ENDED TERMS	c. COSATI Field/Group
Air Pollution Coatings Compliance Calculations Pollution Control Reference Method 24 Test Methods Volatile Organic Compounds	Air Pollution Control	13-B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 15
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

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APPENDIX C

REFERENCE METHOD 24

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475-60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference—see § 60.17).

2.2 ASTM D2369-81, Standard Test Method for Volatile Content of Coatings (incorporated by reference—see § 60.17).

2.3 ASTM D3792-79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference—see § 60.17).

2.4 ASTM D4017-81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference—see § 60.17).

3. *Procedure.*

3.1 Volatile Matter Content. Use the procedure in ASTM D2369-81 (incorporated by reference—see § 60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_s = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_s} \qquad \text{(Eq. 24-1)}$$

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference—see § 60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D1475-60 (Reapproved 1980) (incorporated by reference—see § 60.17).

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v
Water content, W_w	2.9 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter.

4.3 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures

cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropirate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_v, use the lower confidence limits, and for W_w, use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-2}$$

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-4}$$

Where: W_s = Weight solids, g/g.

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PRINTING INKS AND RELATED COATINGS

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.

1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

2. *Procedure.*

2.1 Weight Fraction VOC.

2.1.1 Apparatus.

2.1.1.1 Weighing Dishes. Aluminum foil, 58 mm in diameter by 18 mm high, with a flat bottom. There must be at least three weighing dishes per sample.

2.1.1.2 Disposable syringe, 5 ml.

2.1.1.3 Analytical Balance. To measure to within 0.1 mg.

2.1.1.4 Oven. Vacuum oven capable of maintaining a temperature of 120±2°C and an absolute pressure of 510 ±51 mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2°C for 24 hours.

2.1.1.5 Analysis. Shake or mix the sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{wd}).

Using a 5-ml syringe without a needle remove a sample of the coating. Weigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{sw}). Transfer 1 to 3 g of the sample to the tared weighing dish. Reweigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{sw}). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of 510 ±51 mm Hg and a temperature of 120 ±2°C for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of 120 ±2°C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{ws}). Repeat this procedure for a total of three determinations for each sample.

2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D 1475-60 (Reapproved 1980), which is incorporated by reference. It is available from the American Society of Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. It is also available for inspection at the Office of the Federal Register, Room 8401, 1100 L Street, NW., Washington, D.C. This incorporation by reference was approved by the Director of the Federal Register on November 8, 1982. This material is incorporated as it exists on the date of approval and a notice of any change in these materials will be published in the FEDERAL REGISTER.

2.3 Solvent Density. Determine the density of the solvent according to the procedure outlined in ASTM D 1475-60 (reapproved 1980). Make a total of three determinations for each coating. Report the density D_s as the arithmetic average of the three determinations.

3. *Calculations.*

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content W_o using the following equation:

$$W_o = \frac{M_{o1} + M_{cv1} - M_{cv2} - M_{o2}}{M_{cv1} - M_{cv2}}$$

(Eq. 24A-1)

Report the weight fraction VOC $\overline{W}_o$ as the arithmetic average of the three determinations.

3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content V_o using the following equation:

$$W_o = \frac{M_{v1} + M_{cv1} - M_{cv2} - M_{v2}}{M_{cv1} - M_{cv2}} \qquad \text{Eq.24A-1}$$

$$V_o + \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

4. *Bibliography.*

4.1 Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475-60 (Reapproved 1980).

4.2 Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R. A., Radian Corporation. September 25, 1979. Gravure Ink Analysis.

4.3 Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979. Gravure Ink Analysis.

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16. ABSTRACT

The calculation of volatile organic compound emissions from surface coating operations to determine compliance is often a complicated task, sometimes creating confusion with compliance authorities and sources alike. In an attempt to minimize this confusion, EPA (OAQPS) has periodically issued guidance in this area, generally in the form of memoranda to the EPA Regional Offices. The most recent document is entitled "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings," published December 1984, EPA 450/3-84-019.

"A Guideline for Surface Coating Calculations" takes the above guidance process one step further for surface coating operations. Guidance is provided on how to compute existing and allowed emissions based on the above document as well as previously issued Control Technique Guidelines for the individual categories. Example calculations are included for basic emission problems, compliance determinations, equivalency determinations, application of transfer efficiency, and calculations involving complex multiproduct plants. The appropriate data sheets, a list of various equations and notations, and graphs and tables useful in making the above calculations are also included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Surface Coating VOC Data Sheets Calculations Compliance Determination Control Strategy Evaluation	Air Pollution Control Organic Chemicals Coating Operations	

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Air

APTI Course SI:417 Controlling VOC Emissions from Leaking Process Equipment

Student Guidebook

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Office of Air Quality Planning and Standards
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Lesson 1

Controlling VOC Emissions from Leaking Process Equipment

Course Overview

Course Description

This course is designed for technical people involved in monitoring industries for VOC emissions from leaking process equipment. The course reviews in detail the sources of fugitive VOC emissions and the procedures and equipment used to detect leaks. Course topics include:

Introduction to source categories and regulations
Potential sources of emissions
Inspection procedures
Devices used to detect leaking components
Equipment and procedures used to control leaks

Course Goal and Objectives

Goal

To familiarize you with the sources of VOC emissions and with methods used to detect and control leaks.

Objectives

Upon completion of this course, you should be able to:

1. describe what **constitutes a leak.**
2. recognize five major components that may leak.
3. identify control techniques and hardware used to prevent components from leaking.
4. name three methods used to detect leaks.
5. describe the procedures for using a portable VOC detector to detect a leaking component.
6. describe the operation of two portable VOC detection devices.

Lesson Titles

Lesson 1: Course Overview
Lesson 2: Background for Fugitive VOC Emission Regulations
Lesson 3: Potential Sources of Fugitive VOC Emissions
Lesson 4: Control of Fugitive VOC Emissions from Process Equipment
Lesson 5: Portable VOC Detection Devices
Lesson 6: Inspection Procedures

Requirements for Successful Completion of this Course

In order to receive 2.0 Continuing Education Units (CEUs) and a certificate of course completion, you must:

1. take one mail-in final examination.
2. achieve a final course grade of at least 70% based on the final examination.

Materials

SI:417 Guidebook, *Controlling VOC Emissions from Leaking Process Equipment*
SI:417 Final exam; 40 questions

The content of some of the lessons in this guidebook has been adapted from EPA documents. The applicable documents are referenced at the end of these lessons.

Use of the Guidebook

This guidebook directs your progress through the text material for this course. This first lesson introduces the rest of the course material and explains how to use it. Lessons 2 through 6 are self-paced in a text format that provides review exercises for sections of each lesson. To complete a review exercise, place a piece of paper across the page covering the questions below the one you are answering. After answering the question, slide the paper down to uncover the next question. The answer to the first question will be given on the right of the page separated by a line from the second question (Figure 1-1). All answers for review questions will appear below and to the right of their respective questions. The answers will be numbered to match the questions.

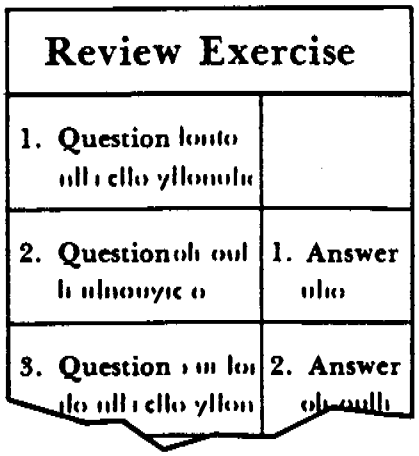


Figure 1-1. Review exercise format.

Complete the review exercise for each section in each lesson. If you are unsure about a question or answer, review the lesson section preceding the question. Then proceed to the next section.

Lesson Content

Lessons in this guidebook contain the following information:

- lesson goal
- lesson objectives
- text material
- review exercises and exercise answers

Instructions for Completing the Final Examination

Contact the Air Pollution Training Institute if you have any questions about the course or when you are ready to receive a copy of the final examination.

After completing the final exam, return it and the answer sheet to the Air Pollution Training Institute. The final exam grade and course grade will be mailed to you.

Air Pollution Training Institute
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MD 20
Research Triangle Park, NC 27711

Lesson 2

Background for Fugitive VOC Emission Regulations

Lesson Goal and Objectives

Goal

To familiarize you with the regulations and terminology used when controlling VOC leaks from process components such as valves, pump seals, and compressor seals.

Objectives

Upon completing this lesson, you should be able to:

1. define what constitutes a leaking component.
2. list three industries which have considered, proposed, or promulgated regulations to reduce fugitive VOC emissions.
3. state the difference between CTG, NSPS, and NESHAPs.

Introduction

The National Ambient Air Quality Standards (NAAQS) for Ozone (O_3) were revised on February 8, 1979. Ozone is seldom emitted directly into the atmosphere, but results primarily from a series of complex chemical reactions between organic compounds and nitrogen oxides in the presence of sunlight. In order to meet the NAAQS, the Clean Air Act requires States to promulgate regulations which will limit the amount of organic compounds that can be emitted from various sources.

Major sources of hydrocarbon emissions were identified and placed on the EPA priority list. The list ranks source categories in terms of the quantities of nationwide pollutant emissions, the mobility and competitive nature of each source category, and the anticipated danger to public health or welfare. Two categories that specifically address fugitive emission sources appear on the list: petroleum refineries and synthetic organic chemicals manufacturing (SOCMI). Other source categories also address fugitive emissions. *Fugitive emissions* are those volatile organic compounds (VOCs) released into the atmosphere when the gaseous or liquid hydrocarbon fluid that is being processed leaks from plant equipment or is exposed to the atmosphere. Pump seals, compressor seals, valves and flanges are a few samples of process equipment that may leak; while cooling towers, wastewater treatment and separating systems are examples of potential fugitive

emissions sources due to exposure. Table 2-1 lists the industries for which standards or guidelines governing fugitive emissions are being considered, proposed, or promulgated.

Table 2-1. Source categories that emit fugitive VOCs.

Source category	Type of control guidance
Petroleum refineries	CTG*, NSPS*
Synthetic organic chemicals manufacturing industry	CTG, NSPS
Polymers and resin manufacturing	CTG, NSPS
Natural gas and natural gasoline processing plants	CTG, NSPS
Benzene in coke ovens/by-products plants	NESHAPs*
Vinyl chloride sources	NESHAPs
Benzene fugitive sources	NESHAPs

*CTG: Control Technique Guidelines
NSPS: New Source Performance Standards
NESHAPs: National Emission Standards for Hazardous Air Pollutants

As can be seen from Table 2-1, there are numerous industries that emit fugitive VOCs. However, the sources of fugitive emissions, methods by which emissions are detected and repaired, and control procedures are very similar for each of these industries. This self-instructional course presents information about the inspection and control of VOC emissions from various pieces of process equipment. Generally, the information presented will apply to process equipment regardless of industry. However, most of the information is based on data from petroleum refineries and synthetic organic chemical manufacturing industries (SOCMI).

Review Exercise

1. True or False? Ozone is emitted from many refineries, chemical plants, and other industries that process hydrocarbons.	
2. True or False? The EPA develops its Priority List for ranking emission sources based only on the amount of pollutants emitted.	1. b. False
3. True or False? Sources of fugitive VOC emissions vary greatly depending on the type of industry.	2. b. False
	3. b. False

Regulations

Two types of Federal regulations pertain directly to fugitive VOC emissions. The regulations are the New Source Performance Standards (NSPS) and the National Emission Standards for Hazardous Air Pollutants (NESHAPs). The Federal Government also publishes Control Technique Guidelines (CTG); the guideline documents are not regulations, but only serve as an information base from which State and local agencies can develop their own regulations. In the past, most State and local agencies have adopted regulations very similar to the CTG documents. However, these agencies have adopted different regulations when local sources have needed special attention.

NSPS apply to all new stationary sources, the construction or modification of which commences after the regulations are proposed by publication in the *Federal Register*. Regulations developed by States (from the CTG) apply to all existing stationary sources, but generally only in areas that are nonattainment for that particular pollutant (in this case O_3). The NESHAPs regulations apply to both new and existing stationary sources, no matter where they are located. With three different regulatory levels, some overlap occurs. In these cases, the most stringent of the regulations apply.

Regulations for controlling fugitive emissions from the various industries listed in Table 2-1 are similar. The regulations all require:

1. use of specific equipment or the inspection of processing equipment at various predetermined time intervals.
2. provisions for repair of leaks and maintenance of equipment.

The main difference between regulations for the various industries is in the frequency that a piece of process equipment must be monitored to detect leaks. In some cases, especially under the NESHAPs and NSPS, additional equipment may be specified to ensure leak-proof operation.

No attempt is made in this course to cover the specific regulations governing each of the seven source categories listed in Table 2-1.

Glossary

The following are a few of the important terms used when discussing fugitive VOC emissions:

Action level—A measured concentration value obtained with a portable VOC monitor. It indicates the need for repair.

Directed maintenance—Refers to a maintenance procedure in which the hydrocarbon detector is used during maintenance. The leak is monitored with the instrument until the repair reduces the measured concentration below the action level.

Fugitive emissions of VOC—Generally refers to the diffuse release of vaporized hydrocarbon or other organic compounds. Fugitive emissions originate from equipment leaks and from large and/or diffuse sources.

Leak—A measured VOC concentration of the action level or greater, determined at a specified distance from the fugitive emission source (usually 0 cm). The concentration

value that defines a leak can vary, depending on the regulation and the industry. A value of 10,000 parts per million by volume (ppmv) is by far the most often used and will be used in this course unless otherwise noted.

No detectable emission—A local VOC concentration at the surface of a source that indicates that a VOC emission (leak) is not present. Since background VOC concentration may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on a meter reading of less than 5% of the leak definition concentration indicates that a VOC emission is not present.

Process stream—Process fluids such as reactants, intermediate products, final products, and by-products, that are contained within pipes, pumps, valves, etc. in a process unit. Steam, water, air, and other utility lines are not considered to be process streams.

Process unit—Equipment assembled to produce an organic chemical as an intermediate or final product. A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the final product.

Repair—Adjustment or alteration of leaking equipment which reduces the screening value from greater than or equal to the action level (i.e., $\geq$10,000 ppmv) to below the action level (i.e., $<$10,000 ppmv).

Response factor—A correction factor that quantifies the difference in meter response that a portable VOC analyzer has for various hydrocarbons and substituted organic chemicals.

Screening—The act of measuring the hydrocarbon concentration of a source with a portable hydrocarbon detector.

Screening value—The hydrocarbon concentration (in ppmv) detected at a source with a portable hydrocarbon detector while traversing with the instrument probe around all the potential leak points of the source.

Source type—Process unit equipment components that may emit fugitive emissions. Common source types of fugitive emissions are valves, pump seals, flanges, compressor seals, and sampling lines.

Type of service—The physical state (gas, liquid, or both) of the material(s) contained in a specific pipeline or vessel. The terms liquid and gas are defined at operating condition of the process. Liquid process streams can be further subdivided into:

- light VOC liquid—any process stream with a vapor pressure of equal to or greater than 0.3 kPa at 20 °C (lighter than kerosene).
- heavy VOC liquid—any process stream with a vapor pressure less than 0.3 kPa at 20 °C.

Volatile organic compound (VOC)—Any organic compound that participates in atmospheric photochemical reactions.

Review Exercise

1. Which of the following does not by itself constitute a regulatory requirement? a. NSPS b. NESHAPs c. CTG d. State or local regulations	
2. The NSPS apply to all new stationary sources a. in an attainment area. b. in a nonattainment area. c. regardless of location.	1. c. CTG
3. True or False? VOC refers to any organic compound that participates in atmospheric photochemical reactions.	2. c. regardless of location.
4. The type of liquid service is usually classified as light or heavy liquid depending on the vapor pressure of the liquid. For example, a liquid with a vapor pressure greater than 0.3 kPa at 20 °C is classified as a a. heavy liquid. b. light liquid.	3. True
5. The vaporized hydrocarbons or other organic compounds that leak from process equipment in chemical plants, petroleum refineries, and other industries are called _____.	4. b. light liquid.
	5. fugitive emissions.

Reference

Environmental Protection Agency (EPA). May 1981. *Evaluation of Maintenance for Fugitive VOC Emissions Control.* EPA 600/2-81-080.

Lesson 3

Potential Sources of Fugitive VOC Emissions

Lesson Goal and Objectives

Goal

To familiarize you with the sources of VOC leaks from process equipment.

Objectives

Upon completing this lesson, you should be able to:

1. recognize at least three types of process equipment that may potentially leak.
2. describe the potential leak areas for the above three sources.
3. recognize leak rate emission factors and the limitations on these using references such as AP-42.

Introduction

There are many potential sources of fugitive VOC emissions. The sources that will be considered in this lesson include: pump seals, compressor seals, process valves, pressure relief devices, and agitator seals. The operation of these sources and their potential leak areas will also be presented in this lesson. Control measures for these sources are presented in the next lesson.

VOC emissions result not only from leaking process equipment, but also from direct exposure of hydrocarbons to the atmosphere. Sampling systems, drains and waste water systems, and

cooling towers all release fugitive hydrocarbons to the atmosphere. A discussion of the control technology for these sources as well as for flanges will be presented in this lesson.

Process Equipment—Leaks

Pumps

Pumps are used extensively by industries to move organic liquids. The most widely used pump is the centrifugal pump. Other pumps used are the positive displacement, reciprocating and rotary action, canned-motor, and diaphragm pumps. Most pumps have a moving shaft which is exposed to the atmosphere (Figure 3-1). The fluid being moved inside a pump must be isolated from the atmosphere. This requires a seal. Leaks can occur at the point of contact between the moving shaft and stationary casing. The canned-motor and diaphragm pumps do not have seals. Therefore, they effectively prevent leaks.

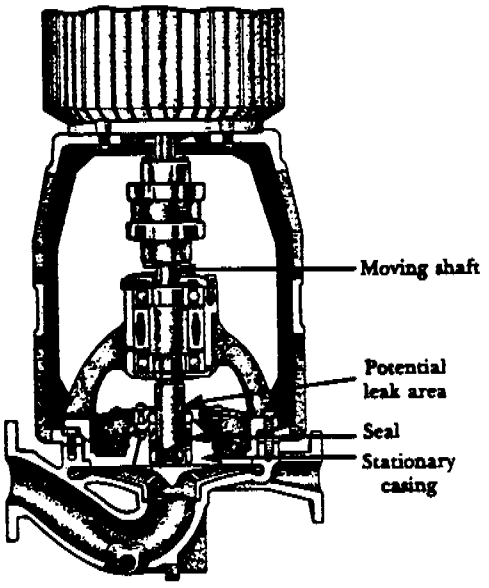


Figure 3-1a. Vertical centrifugal pump.

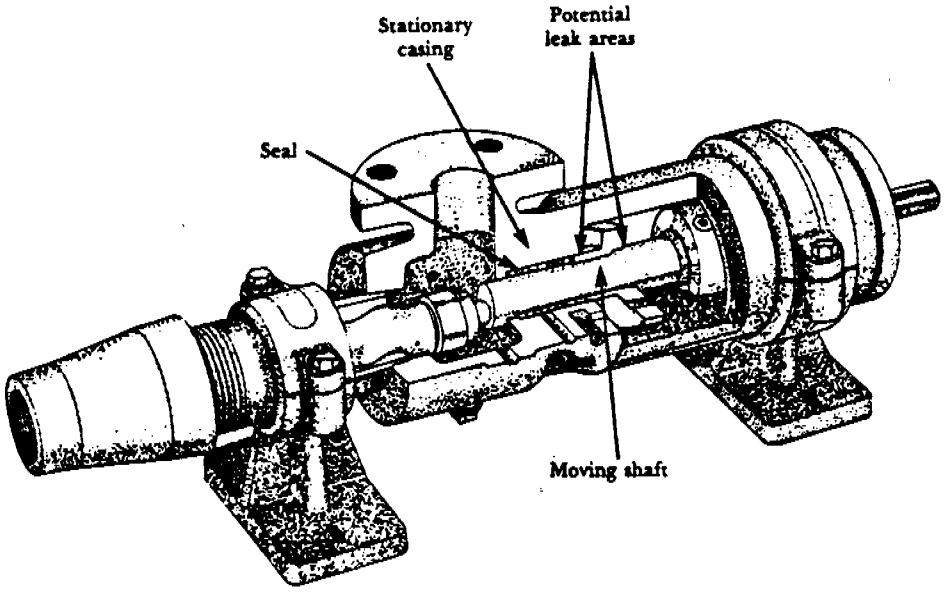


Figure 3-1b. Horizontal pump.

Pump Seals

Two generic seals currently in use on pumps are the packed seal and the mechanical seal. Mechanical seals, the predominant seals in use today, can be categorized as single or double mechanical seals. Single mechanical seals are less effective than double mechanical seals.

Packed Seals

Figure 3-2 is a diagram of a packed seal. Packed seals can be used on both reciprocating and centrifugal (rotary action) pumps. Centrifugal pumps are more widely used. The packing material is compressed in the cavity (stuffing box) to form a seal around the moving drive shaft. A packing gland is used to apply the needed compression. Lubrication is required to prevent frictional heat buildup between the seal and the shaft. A sufficient amount of either the liquid being pumped or a supplementary liquid must be allowed to flow between the packing and the shaft to provide the necessary lubrication.

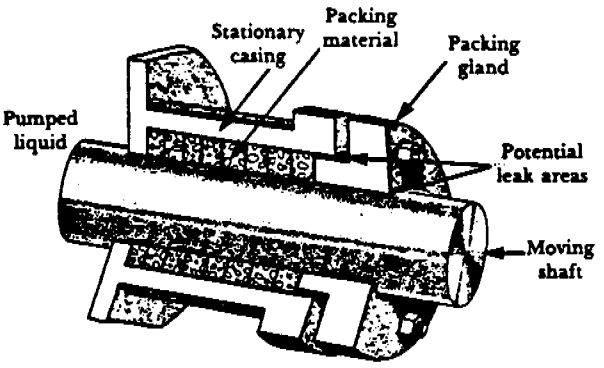


Figure 3-2. Simple packed seal.

Single Mechanical Seals

Figure 3-3 is a diagram of a basic, single mechanical seal. A mechanical seal prevents leakage by means of two sealing elements, one stationary and one rotating. The two sealing elements are also referred to as the primary ring (usually the rotating one) and the mating ring (stationary). The surfaces or faces where the two rings contact are polished (lapped) to a very high degree of flatness to maintain contact over their entire material surface, providing a nearly complete seal. Note that the sealing faces are perpendicular to the shaft rather than parallel to it as in the packed seal.

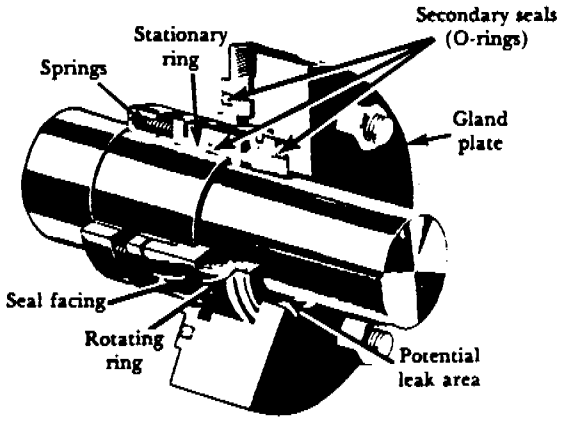


Figure 3-3. Single mechanical seal.

Mechanical seals can also be equipped with secondary seals. Secondary seals prevent leakage between the rotating ring and shaft, the stationary ring and gland plate, and the stuffing box housing and gland ring. The secondary seals are often flexible O-rings, as pictured in Figure 3-3.

Mechanical seals, even equipped with secondary seals, are not leak-proof. As with packed seals, the seal faces must be lubricated to remove frictional heat. Depending on the condition of the seal and degree of flatness of the seal faces, the leakage rate can be very low. The seal coolant is usually the pumped liquid. If it is a poor lubricant, other fluids compatible with the liquid being pumped are used.

Double or Dual Mechanical Seals

Double mechanical seals are generally more effective in preventing leaks than are single seals. Double mechanical seals can be arranged either back-to-back or in tandem. There is a closed cavity between the two seals in a back-to-back arrangement (Figure 3-4). A seal liquid, such as oil or water, is circulated through this seal-housing cavity. In order for the seal to function, the seal liquid must be at a pressure greater than the operating pressure of the liquid being pumped at the stuffing box. As a result some liquid will leak across the seal faces passing into the stuffing box and also out past the outer seal face to the atmosphere. The seal liquid should be non-contaminating so that it will not contaminate either the pumped liquid or the atmosphere.

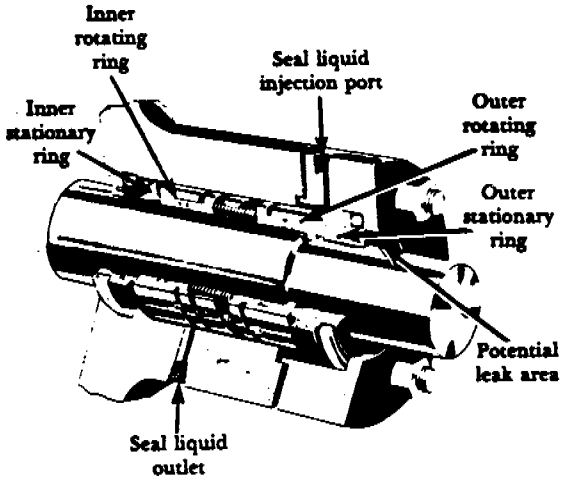


Figure 3-4. Double mechanical seal (back-to-back arrangement).

In the tandem mechanical seal arrangement (Figure 3-5), both seals face the same direction. The inner seal is located in the stuffing box housing rather than in the seal housing. The liquid used for lubrication is referred to as the barrier fluid and is kept at a lower pressure than the fluid in the stuffing box. Therefore, any leakage will be from the stuffing box into the seal cavity containing the barrier fluid. The barrier fluid is routed to a closed reservoir, and any process fluid that has leaked into the seal cavity will also be transferred to the reservoir. To ensure that no VOCs leak from the reservoir, the reservoir can be vented to a control device.

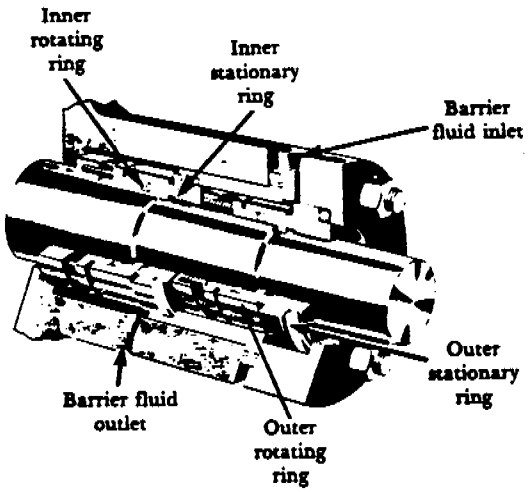


Figure 3-5. Tandem mechanical seal arrangement.

Sealless Pumps

Another pump that has been used is the sealless (or shaftless) pump, which includes the canned-motor pump and the diaphragm pump. In a

canned-motor pump, the cavity that houses the motor rotor and the pump casing are interconnected. As a result, the motor bearings operate in the process liquid. All seals are eliminated. Because the process liquid also lubricates the bearings, abrasive solids cannot be tolerated. Canned-motor pumps are being widely used for handling organic solvents, organic heat transfer liquids, light oils, and many toxic or hazardous liquids. They are also used where leakage is an economic problem.

Diaphragm pumps (Figure 3-6) perform somewhat like piston and plunger pumps. However, the driving member is a flexible diaphragm made of metal, rubber, or plastic. Their primary advantage is the elimination of all packing and seals exposed to the process liquid. This is an important asset when hazardous or toxic liquids are handled.

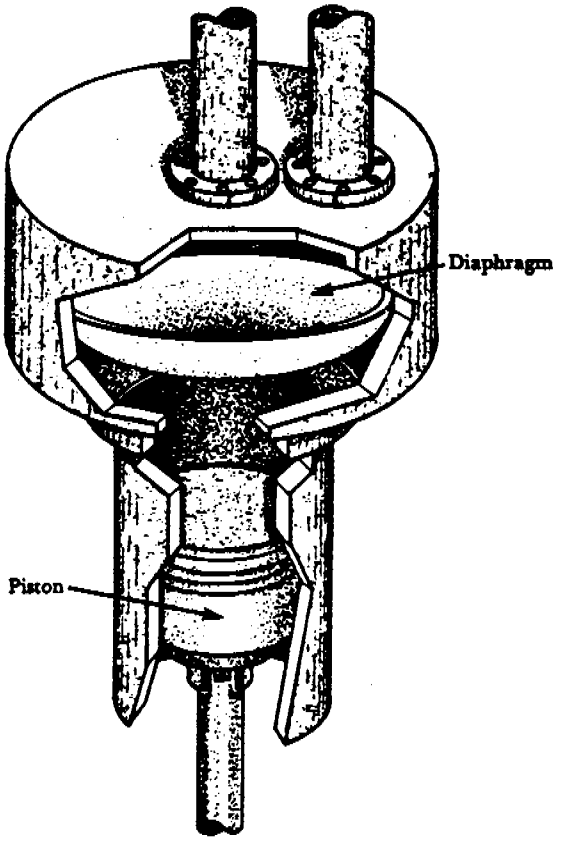


Figure 3-6. Diaphragm pump.

Compressors

Compressors are, basically, pumps that are used in gas service. Gas compressors used in process units can be driven by rotary or reciprocating shafts and therefore need shaft seals to isolate the process gas from the atmosphere. Rotary shafts may use either packed or mechanical seals, while reciprocating shafts must use packed seals. As with the seals in pumps, the seals in compressors are likely to be the source of fugitive emissions from compressors.

Compressor Seals

Shaft seals for compressors may be labyrinth seals, restrictive carbon ring seals, liquid film seals, or mechanical contact seals. All of these seals are leak restriction devices; none of them completely eliminate leakage. Many compressors may be equipped with ports in the seal area to evacuate gases collecting there. If vented to the atmosphere these ports can be a source of fugitive emissions.

Labyrinth Seals

The labyrinth compressor seal is composed of a series of close tolerance, interlocking *teeth* that restrict the flow of gas along the shaft. A straight-pass labyrinth compressor seal is shown in Figure 3-7. Many variations in tooth design and materials of construction are available. Although labyrinth seals have the largest leak potential of the different types, properly applied variations in tooth configuration and shape can reduce leakage by up to 40% over a straight-pass labyrinth seal. However, the loss and recycle rates are usually not acceptable from either environmental or energy conservation standpoints.

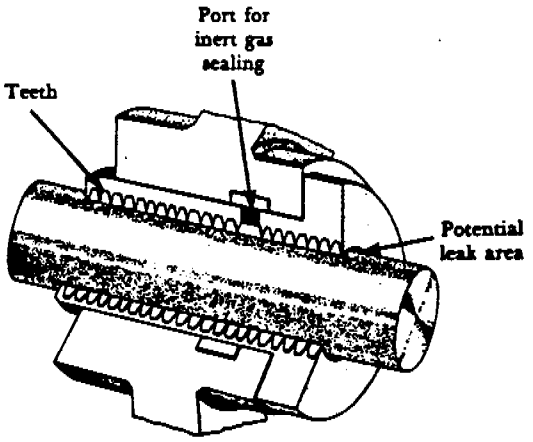


Figure 3-7. Labyrinth shaft seal.

Restrictive Carbon Ring Seals

Restrictive carbon ring seals consist of multiple stationary carbon rings with close shaft clearances. This seal may be operated dry or with a sealing fluid. A restrictive ring seal can achieve lower leak rates than can the labyrinth type.

Liquid Film Seals

Centrifugal compressors can be equipped with liquid film seals. The seal is formed by a film of oil between the rotating shaft and stationary gland. When the circulating oil is returned to the oil reservoir, process gas can be released to the atmosphere. To eliminate release of VOC emissions from the seal oil system, the reservoir can be vented to a control device.

Mechanical Contact Seal

Mechanical contact seals for compressors are similar to the mechanical seals described for pumps. This seal reduces the clearance between the rotating and stationary elements to essentially zero. Oil or another suitable lubricant is applied to the seal faces. Mechanical seals can achieve the lowest leak rates of the seals described here, but they are not suitable for all processing conditions.

Review Exercise

1. Two generic types of seals used on pump shafts are a. single mechanical seals and centrifugal seals. b. packed seals and mechanical seals. c. tandem seals and teeth seals.	
2. Only a _____ seal can be used on both reciprocating and rotary action pumps and compressors. a. packed b. mechanical c. tandem d. centrifugal	1. b. packed seals and mechanical seals.
3. True or False? Unlike packed seals, mechanical seals need no lubrication between the contact faces and therefore totally eliminate all leaks.	2. a. packed
4. True or False? In general, the canned-motor pump and the diaphragm pump have the lowest potential to leak.	3. False
5. True or False? Although all gas compressors are similar in operation to pumps, they have no shafts, and therefore do not leak.	4. True
6. Besides the seal area, two other potential areas where fugitive VOC emissions can be emitted from gas compressors are a. circulating oil reservoirs. b. evacuation ports from seal areas. c. centrifugal ports. d. tandem seals.	5. False
7. A mechanical seal prevents leakage by means of two sealing elements, one _____ and one _____.	6. a. circulating oil reservoirs. b. evacuation ports from seal areas.
	7. stationary (mating) rotating (primary)

Process Valves

One of the most common pieces of equipment in an industrial plant is the valve. Individually, process valves have a low emission rate. However, because of the large number of valves present in most plants, as a group they usually constitute the largest percentage of fugitive VOC emissions (see Appendix D). For example, in a 100,000 gallon per day petroleum refinery, there are usually 25,000 process valves as compared to about 250 pump seals. In some instances valves may make up 90% of the process components that must be checked for leaks.

Many different valves exist, such as globe, gate, plug, ball, and check valves. However, they can be grouped into three functional categories:

- Block: used for on/off control. Generally, these valves are used only occasionally, such as when there is a process change (i.e., unit shutdown).
- Control: used for flow rate control.
- Check: used for directional control. These valves do not have stems, therefore they will not be covered in this course.

The most common valves in use are the gate valve and the globe valve. These valves can be found either in-line or at the end of a process line.

In-line Valves

Valves are activated by a valve stem. Depending on the design, the valve stem may have either a rotational or linear motion. (Pressure relief valves are discussed under a separate heading.) The process fluid inside the valve must be isolated from the atmosphere. This requires a seal. The possibility of a leak through this seal makes it a potential source of fugitive emissions. Figures 3-8 through 3-12 show the potential leak areas from the stems of some common valves. Since check valves are enclosed within process piping, they have no stem or packing gland and are not considered to be a potential source of fugitive emissions.

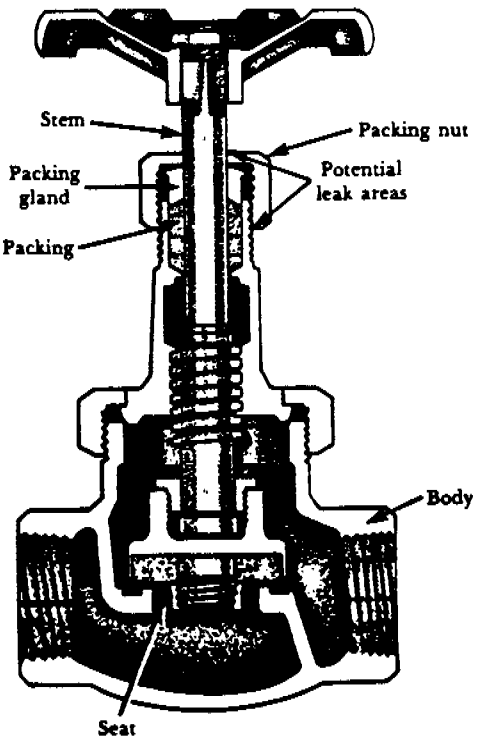


Figure 3-8a. Manual globe valve.

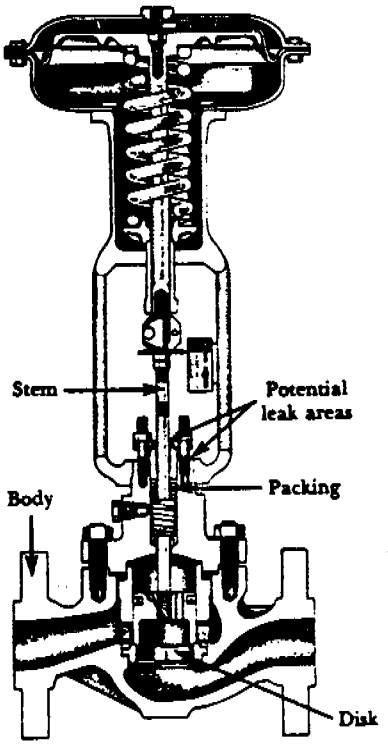


Figure 3-8b. Globe control valve.

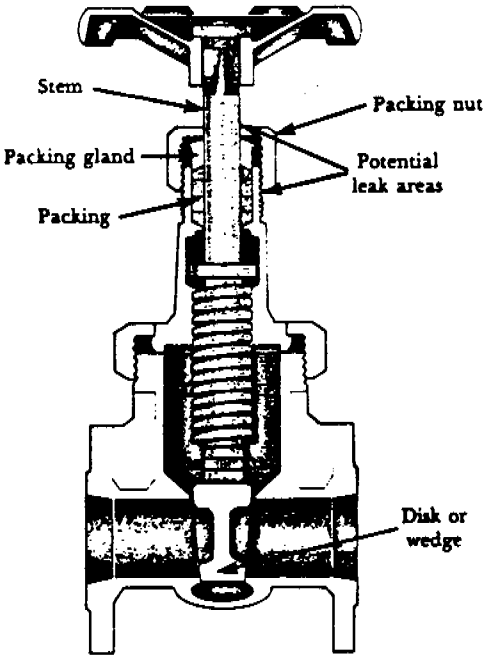


Figure 3-9a. Nonrising stem gate valve.

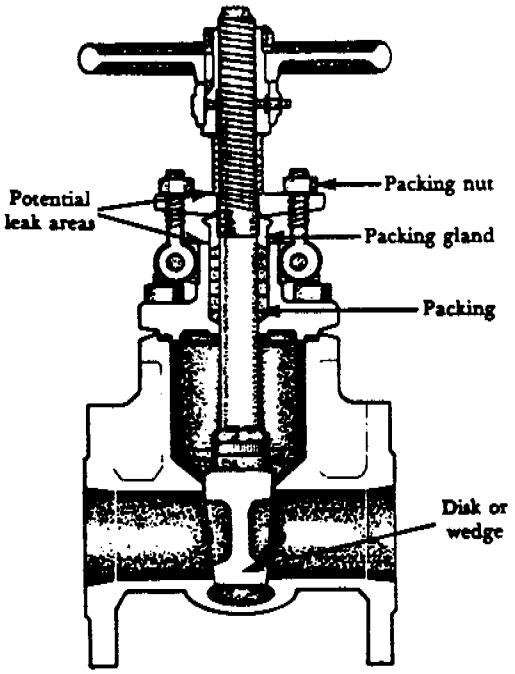


Figure 3-9b. Rising stem gate valve.

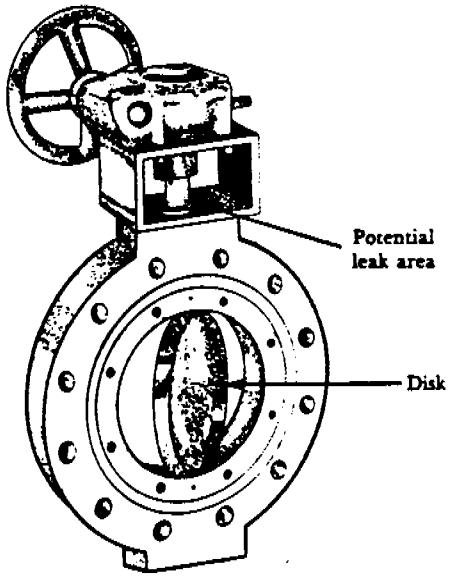


Figure 3-10. Butterfly valve.

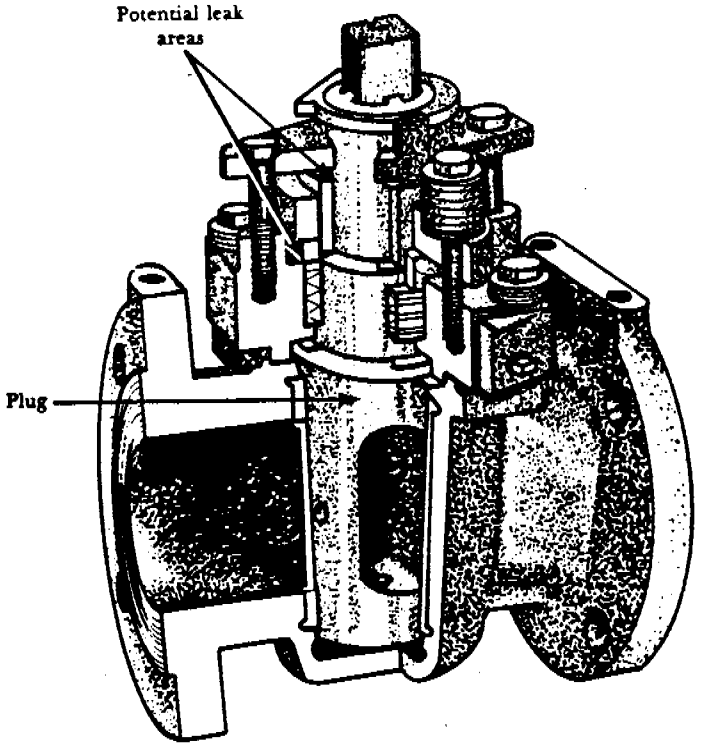


Figure 3-11. Lubricated plug valve.

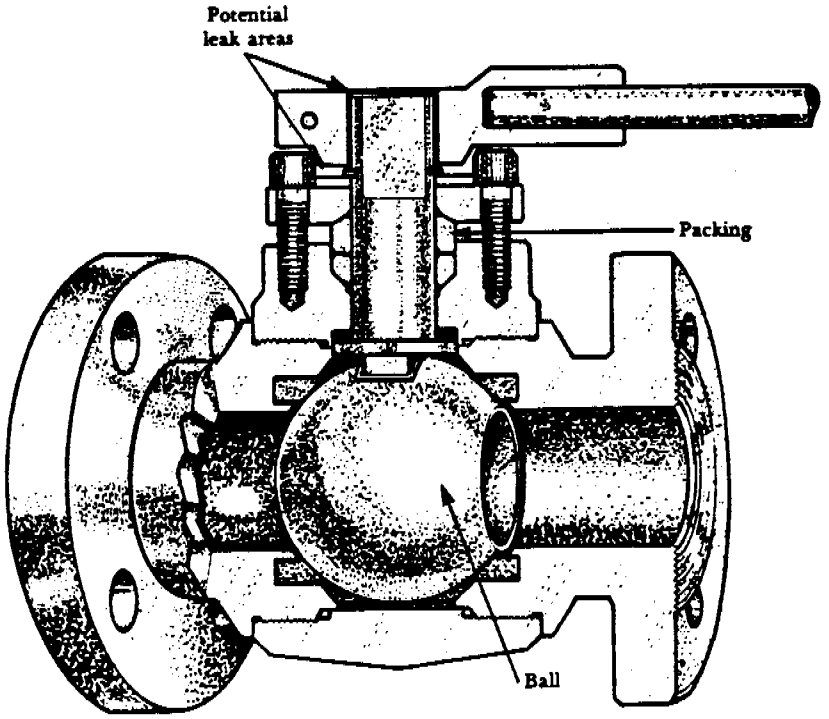


Figure 3-12. Ball valve.

Valve Seals

Sealing the stem to prevent leakage can be achieved by applying *packing* inside a packing gland or O-ring seal. The most common valve-stem seal is the packed seal. A specialized packing material is inserted into the area around the stem, then compressed by a packing gland to form a tight seal. The most common packing materials are various types of braided asbestos that contain lubricants. Other packing materials include graphite, graphite-impregnated fibers, and tetra-fluoroethylene. The packing material used depends upon the valve application and configuration. At high pressures these glands must be quite tight to attain a good seal. As packing wear or lubricant loss occurs, the packing gland must be tightened to continue providing a tight seal.

Elastomeric O-rings are also used for sealing process valves. These O-rings provide a good seal, but are not suitable where there is sliding motion through the packing gland. These seals are rarely used in high pressure service. Operating temperatures are limited by the O-ring material.

Bellows seals are more effective for preventing process fluid leaks than are conventional packing glands or any other gland-seal arrangements. This seal incorporates a formed metal bellows that makes a barrier between the disc and body bonnet joint. An example of this seal is presented in Figure 3-13. The bellows is the weak point of the system and its service life can be quite variable. Consequently, the bellows seal is usually both backed up with a conventional packing gland and often fitted with a leak detector in case the seal fails.

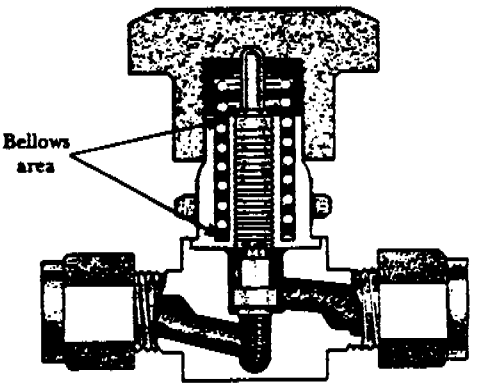


Figure 3-13. Bellows seal.

Specialized valve designs can isolate both the working parts of the valve and the environment from the process liquid. This may be done with a *diaphragm seal*. Figure 3-14 illustrates two diaphragm seals on a globe valve; the bonnet seal and the weir seal. The weir seal's diaphragm may also be used to control the flow of the process fluid. In this design, a compressor component pushes the diaphragm toward the valve bottom, throttling the flow. The diaphragm and compressor are connected so that it is impossible for them to be separated under normal working conditions. When the diaphragm reaches the valve bottom, it seats firmly, forming a leak-proof seal. This configuration is recommended for fluids containing solid particles and for medium-pressure service. These valves can be used at temperatures of up to 205 °C and in severe acid solutions depending upon the diaphragm material used. A valve using a diaphragm seal can become a source of fugitive emissions if that seal fails.

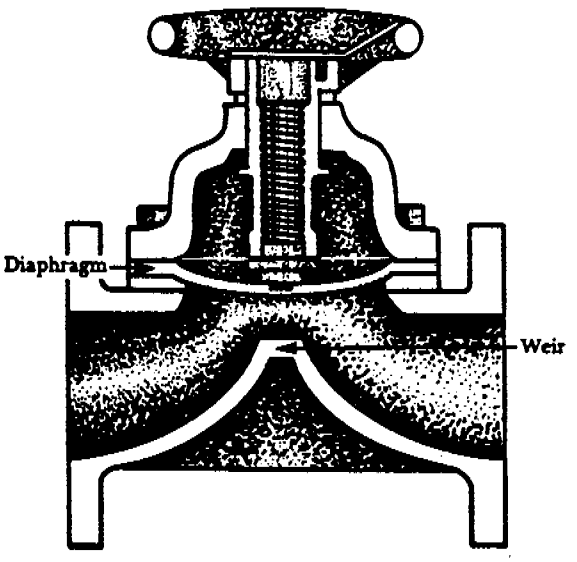


Figure 3-14a. Weir diaphragm seal.

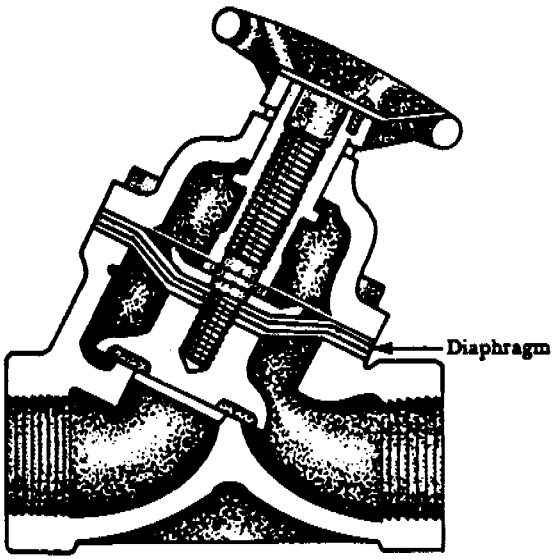


Figure 3-14b. Bonnet diaphragm seal.

Open-ended Valves or Lines

Some valves are installed so that they operate with the downstream line open to the atmosphere. Open-ended valves may be used for draining, venting, or purging. As with the valve stem seal, the valve seat may also be a source of emissions. A faulty valve seat or incompletely closed valve would result in leakage of VOCs to the atmosphere.

Pressure Relief Devices

Engineering codes require that pressure-relieving devices or systems be used in applications where the process pressure may exceed the maximum allowable working pressure of the vessel. The most common pressure-relieving device used in process units is the *pressure relief valve* (Figure 3-15). Typically, a relief valve is spring-loaded. It is designed to open when the process pressure exceeds a set pressure. This allows the release of vapors or liquids until the system pressure is reduced to its normal operating level. When the normal pressure is reattained, the valve reseats, and a seal is again formed. There are two potential causes of leakage from relief valves. One is simmering or popping, which is a condition caused by the system pressure being close to the set pressure of the valve. Simmering occurs when the operating pressure is similar to the set pressure of the valve, while popping occurs when the operating pressure exceeds the set pressure, generally for an extremely short period. The other cause of leakage is improper valve reseating after a relieving operation.

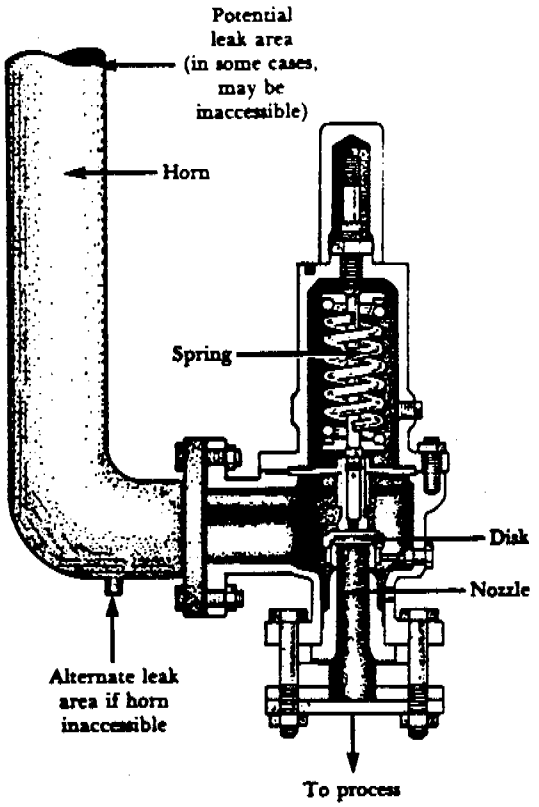


Figure 3-15. Spring loaded pressure relief valve.

Rupture disks are also commonly used on process units. These disks can be used in combination with or in place of pressure relief valves. These disks are made of a material that ruptures when a set pressure is exceeded, thus allowing the system to depressurize. The advantage of a rupture disk is that it seals tightly and does not allow any VOCs to escape from the system under normal operation. However, when the disk does rupture, the system depressurizes until atmospheric conditions are obtained. This could result in an excessive loss of product or a corresponding excessive release of fugitive emissions.

Agitators

Agitators are commonly used to stir or blend chemicals. Like pumps and compressors, agitators may leak organic chemicals at the point where the shaft penetrates the casing. Consequently, seals are required to minimize fugitive emissions from

agitators. Four seals are commonly used with agitators: packed seals, mechanical seals, hydraulic seals, and lip seals.

Agitator Seals

Packed seals for agitators are very similar in design and application to the packed seals for pumps. Although *mechanical seals* are more expensive than the other three seals (packed, hydraulic, or lip), they greatly reduce leakage rate. This offsets their higher cost. Mechanical seals need less frequent maintenance—one-half to one-fourth that of packed seals. In fact, when used on agitators at pressures greater than 1140 kPa (150 psig), mechanical seals are so superior that the use of packed seals is rare. Like packed seals, mechanical seals for agitators are similar in design and application to mechanical seals for pumps.

The *hydraulic seal* (Figure 3-16) is the simplest agitator shaft seal. In the hydraulic seal, an annular cup attached to the process vessel contains a liquid that is in contact with an inverted cup attached to the rotating agitator shaft. The primary advantage of this seal is that it is a non-contact seal. However, this seal is limited to low temperatures and pressures and can handle only very small pressure fluctuations. Organic chemicals may contaminate the seal liquid and then be released into the atmosphere as fugitive emissions. Therefore, the hydraulic seal is the least used agitator seal.

A *lip seal* (Figure 3-17) can be used on a top-entering agitator as a dust or vapor seal. The sealing element is a spring-loaded elastomer. Lip seals are relatively inexpensive and easy to install. Once the seal has been installed, the agitator shaft rotates in continuous contact with the lip seal. Pressure limits of the seal are 2 to 3 psi because it operates without lubrication. Operating temperatures are limited by characteristics of the elastomer. Fugitive VOC emissions could be released through this seal when it wears excessively, or when its pressure limits are surpassed by the operating pressure.

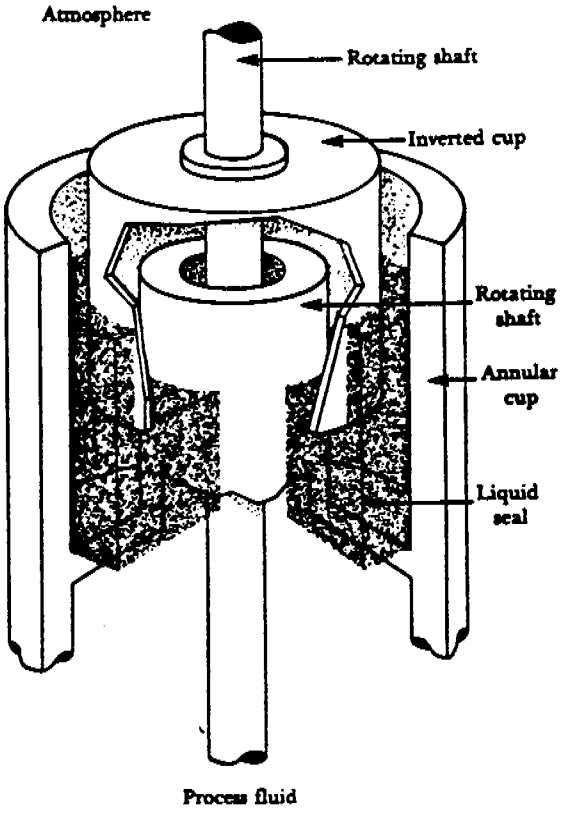


Figure 3-16. Hydraulic seal for agitators.

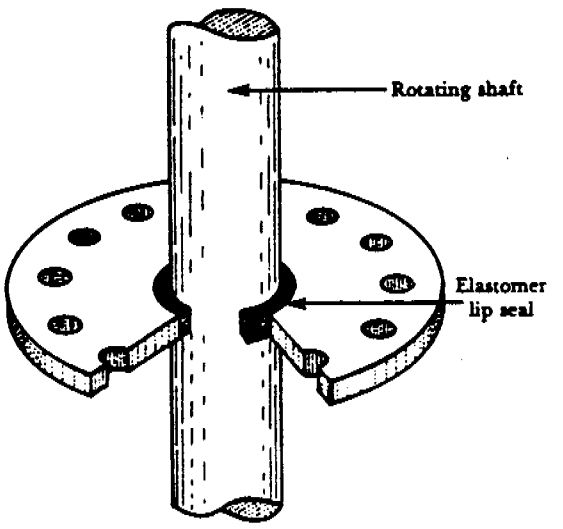


Figure 3-17. Lip seal.

Review Exercise

1. Generally, _____ contribute the largest percentage of fugitive VOC emissions. a. pump seals b. flanges c. valves d. compressor seals	
2. Process valves can leak through the packing around the valve a. stem. b. gate. c. globe. d. check.	1. c. valves
3. Process valves that are used for on/off control when there is a process change are referred to as _____ valves. a. control b. block c. relief d. check	2. a. stem.
4. True or False? Open-ended valves can leak from both the valve stem and the seat.	3. b. block
5. The leakage from relief valves that occurs when the system pressure is too close to the set pressure of the relief valve is known as a. hydraulic or pressure. b. plugging or checking. c. blocking or controlling. d. simmering or popping.	4. True
6. Rupture disks are used in combination with or in place of _____ to prevent leaks. a. pressure relief devices b. pump seals c. compressor seals d. agitators	5. d. simmering or popping
7. _____ are commonly used to blend or stir chemicals. a. Fans b. Spoons c. Agitators d. Valves	6. a. pressure relief devices
	7. c. Agitators

8. True or False? Packed, mechanical, hydraulic, and lip seals are all used to prevent leaks from agitators.	
9. _____ seals can isolate both the working parts of the valve and the environment from the process fluid.	8. True
	9. Diaphgram

Other Potential VOC Emission Sources

Sampling Systems

The operation of a process unit is checked periodically by routine analysis of feedstocks and products. To obtain representative samples for these analyses, sampling lines must be purged before sampling. The purged liquid or vapor is sometimes drained onto the ground or into a sewer drain, where it can evaporate and release VOC emissions to the atmosphere.

Closed-purge sampling can be used to eliminate any possible emissions. Closed-purge sampling systems eliminate VOC emissions either by returning the purge material directly to the process or by collecting the purge in a closed collection system for eventual recycle or disposal.

Flanges

Flanges are bolted, gasket-sealed junctions between sections of pipe and pieces of equipment. They are used wherever pipe or equipment components (vessels, pumps, valves, heat exchangers, etc.) may require isolation or removal. The possibility of a leak through the gasket seal makes them a potential source of fugitive emissions (Figure 3-18).

The results of EPA's refinery sampling programs have shown that flanges have a very low emission factor. Even though there are many of them in any refinery or chemical plant, their overall con-

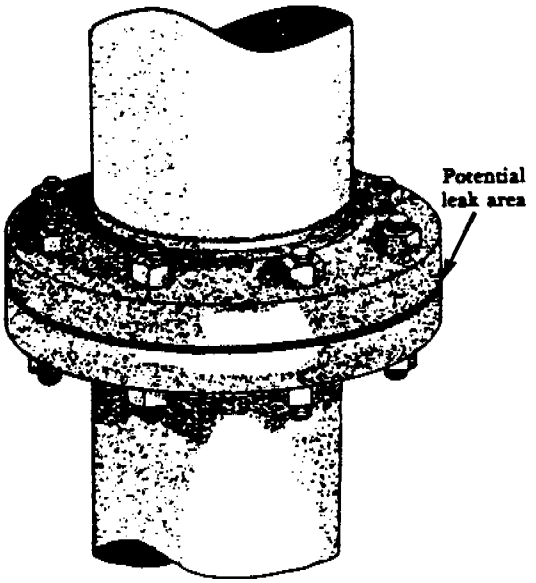


Figure 3-18. Flange.

tribution to the emission rate is small (see Appendix D). Most flanges cannot be isolated from the process to permit gasket replacement. If a flange is found to leak, the only repair options are tightening the flange bolts or injecting a sealing fluid. Similar potential sources of VOCs are any joint connections and moving parts that have seals to keep VOCs from escaping to the atmosphere.

Cooling Towers

Cooling towers remove heat from water used to cool process equipment such as reactors, condensers, or heat exchangers. Cooling water is circulated through the process units (in tubes) and returned to the cooling tower where the water is cooled. In the cooling tower, air is circulated through the water, a portion of the water evaporates into the air and the remaining water is cooled by furnishing the heat for this evaporation process (Figure 3-19).

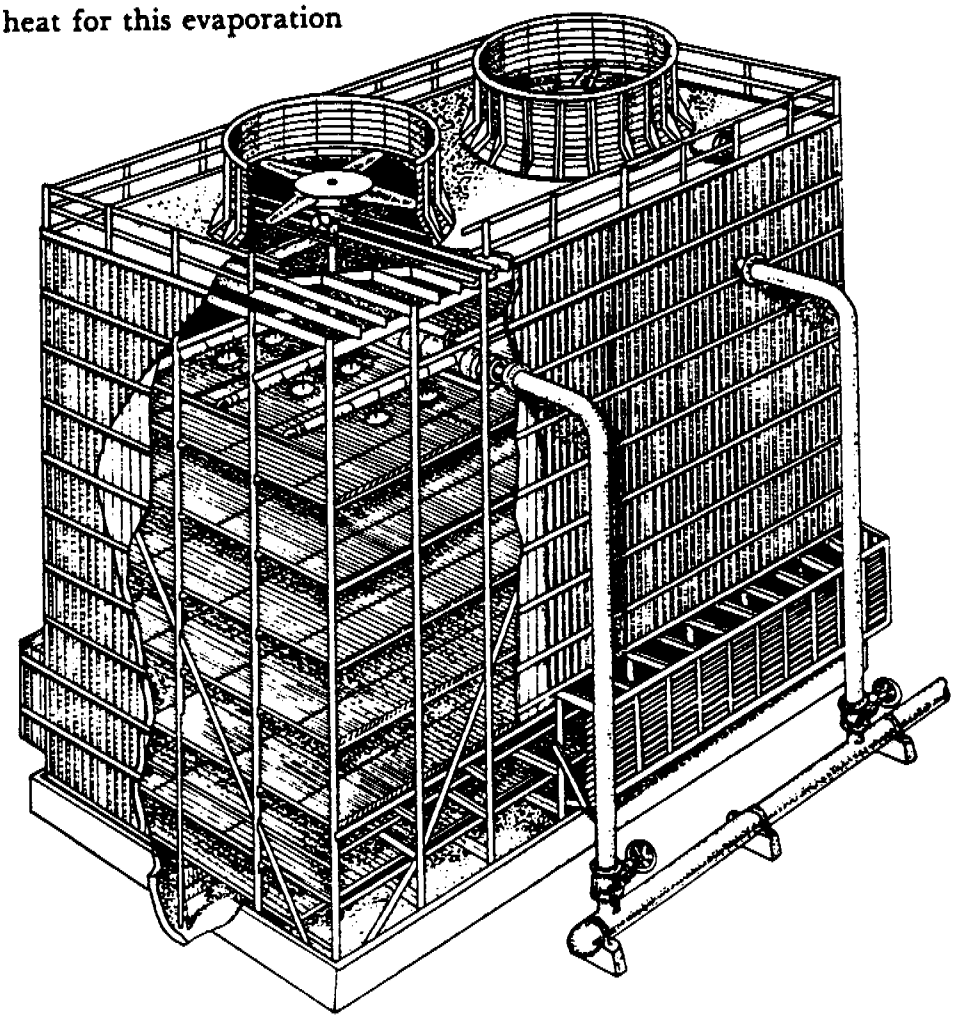


Figure 3-19. Cooling tower.

Organic fluids can enter the cooling water from leaking process equipment or as a result of using contaminated process water as cooling tower make-up water. VOCs can be released to the atmosphere as cooling water vaporizes in the tower.

In a recent survey, the majority of cooling towers tested did not have significant VOC emissions. These cooling towers use indirect (non-contact) condensation which greatly reduces the amount of contaminated cooling water entering the tower. However, if a leak occurs in the process equipment or if direct contact condensation is used, VOC emissions can be significant.

The best control for cooling towers is to minimize the amount of hydrocarbons entering the tower. Direct contact condensation is used in some existing plants, but its use is being phased out because of environmental considerations. Monitoring the hydrocarbon input to the cooling tower is very difficult. Even if elevated concentrations of hydrocarbons are detected, identifying and repairing the specific leak can be very difficult. However, if a leak occurs in the process equipment, it is often in the best interests of the plant to repair it as soon as possible.

Process Drains and Wastewater Systems

Contaminated wastewater can originate from several sources including (but not limited to) leaks, spills, pump and compressor seal cooling and flushing, sampling equipment cleaning, and rain runoff. Contaminated wastewater is collected in the process drain system and directed to the wastewater treatment system where hydrocarbons may be recovered and the wastewater undergoes treatment as required. Organic compounds contained in the wastewater can evaporate wherever wastewater is exposed to the atmosphere. As such, the primary VOC emission points include the drain system vents and the surfaces of forebays and separators.

Several known techniques reduce VOC emissions from process drains and wastewater separators. Process drain emissions can be controlled by reducing the amount of VOC that is spilled or

otherwise put into the drain system. The drains can also be controlled by installing inverted U-bends to trap VOCs within the drain system. Available data show that only a small percentage of drains have concentrations greater than 10,000 ppmv. Wastewater separators can be controlled by covering or enclosing the oily water surface of the separator. Although uncontrolled wastewater separator emissions can be quite large, the results of ongoing studies will need to be reviewed to determine the magnitude of emissions under existing controls.

Emission Factors

Data to quantify the uncontrolled levels of emissions from the various sources presented in this lesson are not available for all the source categories. Data of this type have been obtained for the petroleum refining industry and are presented in Table 3-1. Note that the emission factors in Table 3-1 are the average for all components—both leaking and nonleaking. For example, to compute the emissions from pipeline valves in gas service, multiply 0.059 lb/hr times the total number of valves (in gas service) in the refinery.

In addition, it is important to note that these emission factors were developed from data taken from refineries without inspection and repair programs (outlined in Lesson 4). While these refineries generally repair leaks that are physically evident (to minimize product loss), equipment is not repaired specifically to reduce the level of VOC emissions. Therefore, for refineries that have VOC emissions maintenance and repair programs, the emission factors in Table 3-1 are **not** applicable.

Presently, the EPA is developing a method to better estimate the emission factors from facilities having operation and maintenance programs. (This is also discussed in Lesson 4). The approach taken is to estimate an emission-reduction efficiency based on the following factors:

Theoretical Maximum Control Efficiency—Fraction of total mass emissions for each source type with VOC concentrations greater than the action level.

Leak Occurrence and Recurrence Correction Factor—Correction factor to account for sources which start to leak between inspections (occurrence) and for sources which are found to be leaking, are repaired, and start to leak again before the next inspection (recurrence).

Non-instantaneous Repair Correction Factor—Correction factor to account for emissions which occur between detection of a leak and subsequent repair; that is, repair is not instantaneous.

Imperfect Repair Correction Factor—Correction factor to account for the fact that some sources that are repaired are not reduced to zero emission levels. For computational purposes, all sources that are repaired are assumed to be reduced to a 1000 ppmv emission level equivalent to a concentration of 1000 ppmv.

For further information on this method see EPA, April 1982.

Table 3-1. Fugitive emission factors for petroleum refineries.[a]

Emission source	Process stream type[b]	Emission factor units	Emission factors: Uncontrolled emissions[c]		Emission factors: Controlled emissions	Applicable control technology	Emission factor rating
Pipeline valves	II	lb/hr-source	0.059	(0.030-0.110)	NA	Monitoring and maintenance program	A
		kg/day-source	0.64	(0.32-1.19)			
	III	lb/hr-source	0.024	(0.017-0.036)	NA		A
		kg/day-source	0.26	(0.18-0.39)			
	IV	lb/hr-source	0.0005	(0.0002-0.0015)	NA		A
		kg/day-source	0.005	(0.002-0.016)			
	V	lb/hr-source	0.018	(0.007-0.045)	NA		A
		kg/day-source	0.20	(0.08-0.49)			
Open-ended valves[d]	I	lb/hr-source	0.005	(0.0016-0.016)	NA	Installation of cap or plug on open-end of valve/line	A
		kg/day-source	0.05	(0.017-0.17)			
Flanges	I	lb/hr-source	0.00056	(0.0002-0.0025)	NA	Monitoring and maintenance programs	A
		kg/day-source	0.0061	(0.002-0.027)			
Pump seals	III	lb/hr-source	0.25	(0.16-0.57)	NA	Mechanical seals; dual seals, purged seals monitoring and maintenance programs, controlled degassing vents	A
		kg/day-source	2.7	(1.7-4.0)			
	IV	lb/hr-source	0.046	(0.019-0.11)	NA		A
		kg/day-source	0.50	(0.21-1.2)			
Compressor seals	II	lb/hr-source	1.4	(0.66-2.9)	NA	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlled degassing vents	A
		kg/day-source	15	(7.1-31)			
	V	lb/hr-source	0.11	(0.05-0.23)	NA		A
		kg/day-source	1.2	(0.5-2.5)			
Process drains	I	lb/hr-source	0.070	(0.023-0.20)	NA	Traps and covers	A
		kg/day-source	0.76	(0.25-2.2)			
Pressure vessel relief valves (gas service)[e]	II	lb/hr-source	0.36	(0.10-1.3)	Negligible	Rupture disks upstream of relief valves and/or venting to a flare	A
		kg/day-source	3.9	(1.1-14)			
Cooling towers		lb/10^3 gal cooling water	6		0.70	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D
		kg/10^6 liters cooling water	0.7		0.083		
		lb/10^3 bbl refinery feed[f]	10		1.2		
		kg/10^3 liters refinery feed	0.03		0.004		
Oil/water separators		lb/10^3 gal wastewater	5		0.2	Covered separators and/or vapor recovery systems	D
		kg/10^3 liter wastewater	0.6		0.024		
		lb/10^3 bbl refinery feed	200		10		
		kg/10^3 liters refinery feed	0.6		0.03		

[a] Overall, less than 1% by weight of the total VOC emissions are ethane.
NA = Not Available
A = Excellent
D = Below Average

[b] The volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification numerals and group names and description are:

Stream identification numeral	Stream name	Stream group description
I	All streams	All streams
II	Gas streams	Hydrocarbon gas/vapor at process conditions (containing less than 50% hydrogen, by volume)
III	Light liquid and gas/liquid streams	Liquid or gas/liquid stream with a vapor pressure greater than that of kerosene (>0.1 psia at 100°F or 689 Pa at 38°C), based on the most volatile class present at >20% by volume
IV	Heavy liquid streams	Liquid stream with a vapor pressure equal to or less than that of kerosene (≤0.1 psia at 100°F or 689 Pa at 38°C), based on the most volatile class present at >20% by volume
V	Hydrogen streams	Gas streams containing more than 50% hydrogen by volume

[c] Numbers in parentheses are the upper and lower bounds of the 95% confidence interval for the emission factor.
[d] The downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.
[e] Emission factor for relief valves in gas service is for leakage, not for emissions caused by vessel pressure relief.
[f] Refinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

Review Exercise

1. Fugitive emisisons of VOCs from sampling operations can be controlled by using a(n) _____ sampling system. a. Method 5 b. Method 21 c. closed purge d. open valve	
2. True or False? Although flanges are the most numerous source of fugitive VOC emissions their total mass emission rate is generally very small.	1. c. closed purge
3. True or False? Cooling towers and wastewater systems are not generally sources of fugitive VOC emissions, since any VOCs present will be dissolved in the water.	2. True
4. For cooling towers and wastewater systems, the best control technique is to _____ entering the system.	3. False
5. Wastewater separators can be controlled by _____ the oily water separators. a. covering or enclosing b. agitating c. putting mechanical seals on d. the open burning of	4. limit the hydrocarbons
	5. a. covering or enclosing

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Lesson 4

Control of Fugitive VOC Leaks from Process Equipment

Lesson Goal and Objectives

Goal

To familiarize you with control techniques to reduce fugitive VOC leaks.

Objectives

Upon completing this lesson, you should be able to:

1. name process equipment that is designated as ***leakless***.
2. describe three types of inspection programs used to detect VOC leaks from process equipment.
3. list the advantages and disadvantages of the above three inspection programs.
4. describe repair techniques used for leaking valves, pump seals, compressor seals, pressure relief valves, and flanges.
5. list four factors that determine the effectiveness of an inspection and repair program.

Introduction

A number of different regulatory formats could be used by an agency to control fugitive VOC emissions from leaking process equipment. The regulatory formats can be classified as:

1. Equipment Standard
2. Work Practice
3. Standard of Performance or Emission Standard

Prescribing a performance standard for most fugitive VOC emission sources is not feasible, since measuring emissions (by the bagging technique) from a single source is very difficult and time consuming. The great number of sources and the fact that they are usually spread apart over large areas make such a requirement economically impractical. The only exception to this performance standard regulation would be if the standard is set to allow "no detectable emissions".

Methods for controlling fugitive VOC emissions from leaking process equipment are generally based on equipment standards, work practice, or a combination of both. This lesson is divided into three sections. The first section presents the control devices which can be used to limit fugitive VOC emissions and describes their uses and limitations. The

second section covers leak detection and repair methods (work practice) that can be instituted to reduce fugitive VOC emissions. The third section discusses work practice regulations.

Control Devices

One approach to controlling fugitive VOC emissions from process equipment is to require the use of equipment that limits VOC emissions. This section discusses the kinds of equipment that could be applied and their advantages and disadvantages.

Pumps

Three control alternatives to eliminate leaks from pump seals are: using dual mechanical seals with a pressure indicator on the barrier fluid system, using a sealless pump, or enclosing the seal area and venting the emissions to a control device.

Dual Mechanical Seals

As discussed in Lesson 3, dual mechanical seals are generally more effective than either single mechanical seals or packing in preventing leaks from rotating pumps. Any leaks through the inner seal may be dissolved or suspended in the sealing fluid between the dual seals. The sealing fluid must be a heavy liquid or non-VOC liquid, otherwise the sealing fluid could leak. Emissions of VOCs from the barrier fluid degassing vents can be controlled by a closed-vent system which consists of piping to transport the degassing emissions to a control device (such as a process heater or vapor recovery system). Control effectiveness as high as 100% for a dual mechanical seal and a closed-vent system is possible depending on the effectiveness of the auxilliary control device and on the frequency of mechanical seal failure. Also, the barrier fluid pressure can be kept greater than the operating pressure so that any leaks will be into the process fluid. In these cases, the barrier and process fluids must be compatible.

To assure proper operation of dual mechanical seals with a closed vent degassing system, a pressure or level indicator can be used on the barrier fluid. This indicator would reveal any catastrophic failure of the inner or outer seal, or of the barrier fluid system. The indicator could be monitored in a control room with an alarm to signal failure of the system. If operated in this manner, dual mechanical seals on pumps can normally be exempted from leak detection and repair programs.

Some conditions preclude the use of dual mechanical seals. These seals can be used only on shafts with rotary motion. And, they cannot be used at temperatures above 260°C (500°F).

Sealless Pumps

Sealless pumps, such as the canned-motor and diaphragm pumps, do not have a potential leak area. Therefore, they achieve 100% control. The main limitation of these pumps is that they can pump only clean process fluid. Since a small portion of the process fluid is

pumped through the bearings to provide lubrication, abrasive solids can cause excessive bearing wear. Sealless pumps are also limited in some process applications by the flow rate or pressure at which the pump is required to operate.

As with any other leakless equipment, an initial performance test using Reference Method 21 can verify that the piece of equipment meets a "no detectable emission" limit. This initial verification and annual rechecks are performed to ensure compliance.

Compressors

Fugitive emissions from compressors occur at the junction of a moving shaft and a stationary casing. Emission reductions from compressors may be achieved by improving the seal at the junction, or by collecting and controlling the emissions from the junction.

Mechanical Contact Seals

Mechanical contact seals for compressors are similar to the mechanical seals described for pump applications. Existing compressors may have mechanical contact seals equipped with barrier fluid flush systems. Barrier fluid reservoir degassing vents must be controlled with closed-vent systems as described for pumps. Sometimes a barrier gas may be used to form a buffer between the compressed gas and the atmosphere. This system requires a clean external gas supply that is compatible with the gas being compressed. Contaminated barrier gas must be disposed of properly. The control efficiency for mechanical contact seals depends on the efficiency of the control device and the frequency of seal failures.

Closed-vent Systems and Control Devices

Compressors in some services cannot be fitted with mechanical seals. For these cases, enclosure of the seal area may be a reasonable option. The seal area of a compressor may be enclosed, and the VOC emissions may be routed to a control device through a closed-vent system. However, flow-inducing devices may be required to transport vapors to the control device. Although the formation of explosive mixtures or excessive pressure buildup in the enclosed seal area may prohibit application of this equipment modification to some existing process units, closed-vent systems have been applied to compressor seal areas in petroleum refineries. Several control methods could be used to dispose of VOC emissions collected from compressor seal areas. Incineration, carbon adsorption, and condensation are three control methods that might typically be applied. Control efficiencies of the three methods depend on specific operating characteristics and type of VOC.

Pressure Relief Devices

Rupture Disks

A rupture disk can be installed upstream of a relief valve in order to prevent fugitive emissions through the relief-valve seat. Figure 4-1 is a diagram of a rupture-disk and relief-valve installation. Under normal conditions, the rupture disk seals the system tightly. But if its set pressure is exceeded, it will break and the relief valve will relieve the pressure. This procedure may require the use of a larger size relief valve because of operating codes. Since it's possible that the disk may rupture, the disk/valve combination may also require appropriate piping changes to prevent disk fragments from lodging in the valve, which would keep it from being reseated properly. A block valve upstream of the rupture disk may be required in order to permit in-service replacement of the disk after rupture. If the disk were not replaced, the first overpressure would result in the relief valve being the same as an uncontrolled relief valve—and it might actually be worse since disk fragments may prevent proper reseating of the relief valve. In some plants, installation of a block valve upstream of a pressure relief device is common practice. In others, it is forbidden by operating or safety procedures. Tandem pressure relief devices with a three-way valve can be used to prevent operation without relief protection if block valves are not allowed.

In rupture-disk/relief-valve combinations, some provision for testing the integrity of the disk is necessary. Pressure should not be allowed to build up in the pocket between the disk and the relief valve; otherwise, the disk will not function properly. The pocket must be connected to a pressure indicator, recorder, or alarm. If the process fluid is not hazardous or toxic, a simple bubbler apparatus can be used to test the integrity of the disk by connecting the bubbler to the pocket. The control efficiency of the disk/valve combination is assumed to be 100% for fugitive emissions resulting from improper seating or relief valve simmering. The control efficiency would be lowered if the disk integrity were not maintained or if the disk were not replaced after rupture. The disk/valve combination has no effect on emissions resulting from overpressure relieving. However, the pressure relief device may be vented to a flare system. This provides control for both overpressure occurrences and any leakage that may occur.

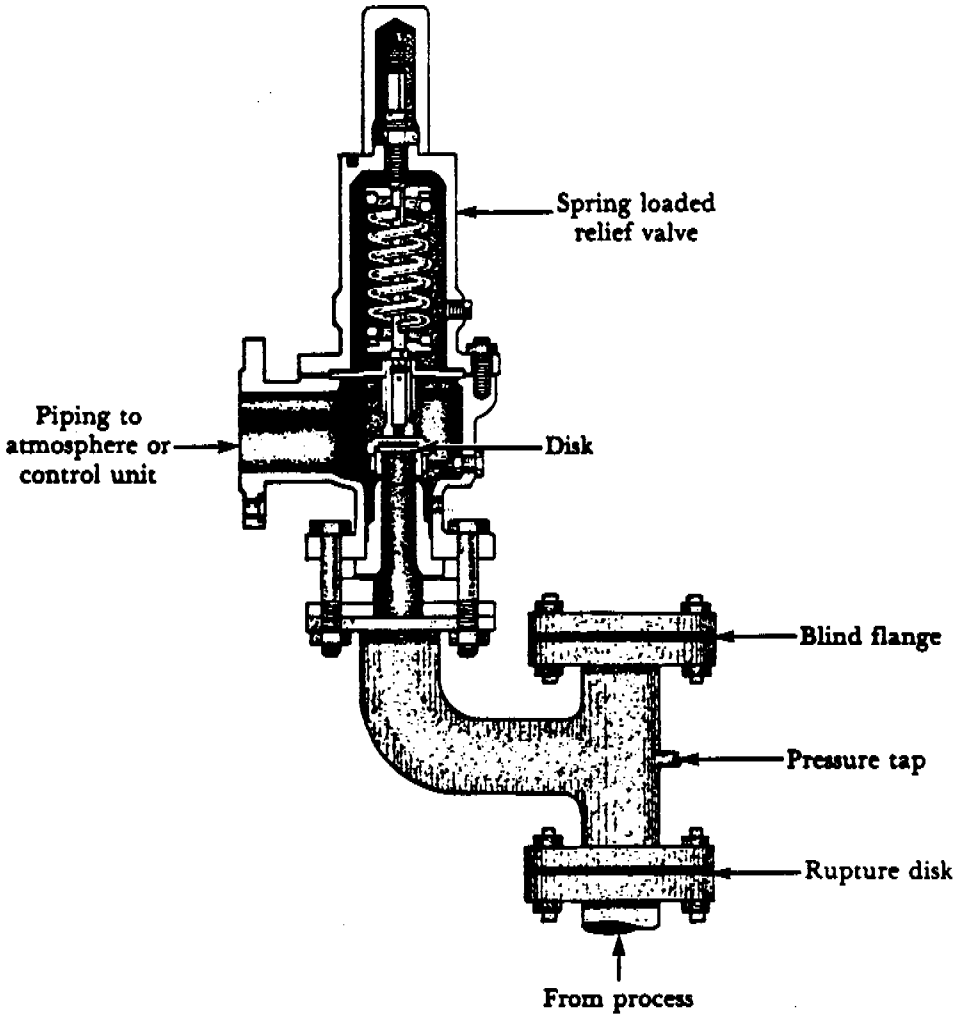


Figure 4-1. Rupture-disk and relief-valve installation.

Open-ended Valves or Lines

Blinds, Caps, and Plugs

Blinds, caps, plugs, or a second valve are devices for closing off the ends of valves and pipes. When installed downstream of an open-ended valve, they prevent leaks that may occur through the seat of the valve from reaching the atmosphere. Open-ended valves are used mostly in intermittent service for sampling, venting, or draining. If a blind, cap, plug, or second valve is used downstream of a valve when it is not in use, VOC emissions can be reduced. If a second valve is used in conjunction with the first valve, the upstream valve should always be closed before the downstream valve is closed. This operational requirement is necessary to prevent the trapping of process fluid between the two valves.

The control efficiency of these devices is assumed to be 100%. The actual control efficiency will depend on how frequently the cap or plug is removed. The installation of a blind, cap, or plug limits, but does not prevent, the leakage that may occur through the valve-stem seal.

Review Exercise

1. The _____ and _____ are two types of sealless pumps, which, because of their design, eliminate areas where leaks can occur.

2. The degassing vents from the barrier fluid on a dual mechanical seal should be
   a. vented to the atmosphere.
   b. equipped with packed seals.
   c. connected to a control system.
   d. bled periodically.

3. Which of the following will **not** prevent emissions from an open-ended valve seat?
   a. packing
   b. cap
   c. plug
   d. second valve

4. True or False? Under normal operating conditions, rupture disks totally prevent the release of any VOC emissions.

5. Of the following, which would be the most effective control equipment for a pump?
   a. single packed seal with pressure indicator for barrier fluid system
   b. dual packed seal with pressure indicator for barrier fluid system
   c. single mechanical seal with pressure indicator for barrier fluid system
   d. dual mechanical seal with pressure indicator for barrier fluid system

1. canned-motor diaphragm

2. c. connected to a control system.

3. a. packing

4. True

5. d. dual mechanical seal with pressure indicator for barrier fluid system

6. True or False? Emissions from compressor seals can sometimes be controlled by enclosing the seal area and venting the emissions to a control device.	
7. Mechanical seals can be used only on shafts that have a(n) _____ motion	6. True
8. True or False? Compressors are essentially pumps used in gas service; therefore, methods to control leaks are similar for both.	7. rotary
9. VOC emissions from open-ended valves can be reduced by installing a _____ a. blind. b. cap. c. second valve. d. all of the above	8. True
	9. d. all of the above

Leak Detection and Repair Techniques

Leak Detection Techniques

Fugitive VOC emissions can be reduced by applying a leak detection and repair program in which fugitive sources are located and repaired at regular time intervals. Leak detection can be accomplished by three monitoring techniques: an individual component survey, a unit area survey, and fixed point monitoring. Only the individual component survey (using a portable VOC detector) has proven effective in locating all significant equipment leaks.

Individual Component Survey

In an individual component survey, each potential fugitive emission source is checked for leakage. The most predominant and effective method of surveying individual components is to use a portable VOC detection device that measures the concentrations at the surface where leakage can occur. This is also commonly referred to as *screening*. Two additional individual component survey methods are: using the visual, auditory, or olfactory senses; and spraying each component with a soap solution and observing bubble formation.

Visual observation is good for locating liquid leaks, especially pump seal failures. For example, observation of liquid leaking along the shaft indicates an outer seal failure. However, observation of a visible leak does not necessarily indicate VOC emissions, since

the leak may be composed of non-VOC compounds or nonvolatile organics. High pressure leaks may be detected by hearing escaping vapors. Leaks of odorous material may be detected by smelling the odor. However, in many instances, even large VOC leaks are not detected by these methods. These methods used by themselves are not adequate to determine compliance, but can indicate which areas should be surveyed with a portable VOC detection device.

Spraying soap solution on equipment components is another individual survey method. If the soap solution forms bubbles or is blown away, a leak from the component is indicated. A disadvantage of this method is that it does not distinguish leaks of non-VOC compounds from VOC leaks. Consequently, air or steam leaks would produce the same observed effect as VOC leaks. This method is only semiquantitative since it requires that the observer subjectively determine the rate of leakage based on the behavior of the soap bubbles. This method is limited to cool sources, since temperatures above 100 °C would cause the water in the soap solution to boil away. To help screen in this temperature range, glycol can be added to the soap solution. This method is also not suited for moving shafts on pumps or compressors, since the motion of the shaft may interfere with the motion of the bubbles caused by a leak. This method can be used in combination with a portable hydrocarbon detector. Where appropriate, the soap solution can be used for an initial screening to limit the number of times the instrument will need to be used. The soap solution will quickly distinguish nonleaks from very large leaks. Leaking sources can then be screened with the detector.

Portable hydrocarbon detection instruments are the best instruments to identify leaks of VOCs from equipment components. This instrument is used to sample and analyze the air close to the potential leak surface by traversing the sampling probe tip over the entire area where leaks may occur. This sampling traverse is referred to as *monitoring* or *screening* The hydrocarbon concentration of the sampled air is displayed on the instrument meter. The performance criteria for monitoring instruments are discussed in Lesson 5. For an individual component, an increased meter reading indicates that an emission or leak is present. Data from petroleum refineries have been used to develop relationships between the monitoring concentration and mass emission rates for several types of sources. However, these correlations are valid only when applied to the average of a large number of sources. The relationship for individual sources between the screening value and the leak rate varies widely. The hydrocarbon concentration that indicates that a component needs maintenance must be chosen. Components which have indicated concentrations higher than this *action level* are marked for repair. Data from petroleum refineries indicate that large variations in mass emission rates may occur over short time periods for an individual component. More frequent monitoring intervals tend to reduce the chance of missing large leaks because of their variable leak rates.

Area Survey

A unit area or walk-through survey entails measuring the ambient VOC concentration within a distance of one meter of all equipment located on the ground or at other accessible levels within a processing area. These measurements are performed with a portable VOC detection instrument that uses a strip chart recorder.

The instrument operator walks a predetermined path to assure total available coverage of a unit on both the upwind and downwind sides of the equipment, noting on the chart record the location in a unit where any elevated VOC concentrations are detected. If an elevated VOC concentration is recorded, the components in that area can be screened individually to locate the specific leaking equipment.

It is estimated that 50% of all significant leaks in a unit are detected by the walk-through survey, provided only a few pieces of equipment are leaking (so that the VOC background concentration is sufficiently reduced to allow reliable detection).

The major advantages of the unit area survey are that leaks from sources near the ground can be located quickly and manpower requirements are lower than those for the individual component survey. Some of the shortcomings of this method are:

1. VOC emissions from adjacent units can cause false leak indications;
2. high or intermittent winds (local meteorological conditions) can increase dispersion of VOC, causing leaks to be undetected;
3. elevated equipment leaks are not detected; and
4. additional effort is necessary to locate the specific leaking equipment (i.e., individual checks in areas where high concentrations are found).

Fixed-point Monitors

This method consists of placing several automatic hydrocarbon sampling and analysis instruments at various locations in the process unit. The instruments may sample the ambient air intermittently or continuously. Elevated hydrocarbon concentrations indicate a leaking component. As in the walk-through method, an individual component survey is required to identify the specific leaking component in the area. For the fixed-point monitoring method, the portable hydrocarbon detector is also required. Leaks from adjacent units and meteorological conditions may affect the results obtained. The efficiency of this method is not well established, but it has been estimated that 33% of the number of leaks identified by a complete individual component survey could be located by fixed-point monitors. These units operate continously. Therefore, they can locate leaks more quickly than individual or unit area surveys. Fixed-point monitors are more expensive than individual source monitors; multiple units may be required; and the portable instrument is also required to locate the specific leaking component. Calibration and maintenance costs may be higher than for individual or area surveys. Fixed-point monitors have been used to detect emissions of hazardous or toxic substances (such as vinyl chloride) as well as potentially explosive conditions. Fixed-point monitors have an advantage in these cases, since a particular compound can be selected as the sampling criterion. In the past, monitoring of this type has been done to determine worker exposure to certain chemicals; not necessarily to limit fugitive emissions of VOCs.

Review Exercise

1. Using a portable VOC detection device to measure the VOC concentration at the surface of a component is commonly referred to as _____.	
2. Visual observation may be an effective technique for locating liquid leaks from _____.	1. screening
3. True or False? Spraying a soap solution on equipment components is the easiest and most effective technique for determining if a component is leaking.	2. pump seals
4. In using a portable hydrocarbon detector, the VOC concentration that indicates that a component needs maintenance is referred to as the _____.	3. False
5. True or False? Walk-through surveys have an advantage over surveying individual components in that the walk-through does not require a portable VOC detector.	4. action level
6. The most effective method for detecting leaking components is a. an individual component survey using a portable VOC detector. b. the area survey using a portable VOC detector. c. fixed-point monitoring. d. visual inspection.	5. False
7. Spraying soap solution to screen for leaking sources should be done only on a. valves. b. flanges. c. cool sources. d. hot sources.	6. a. an individual component survey using a portable VOC detector.
	7. c. cool sources.

Repair Techniques

When leaks are located by the monitoring techniques described in this lesson, the leaking component must be repaired or replaced. Many components can be serviced *on-line*, meaning without interrupting the process. However, a leak that cannot be eliminated by on-line servicing requires that the component be isolated from the process for either repair or replacement. Isolating the component in many instances requires a complete or partial shutdown of the process.

A leaking component may be repaired by either directed or undirected maintenance. *Directed* maintenance is performed while simultaneously monitoring the leaking component with a portable VOC detection device to assess the effectiveness of the repair effort. *Undirected* maintenance refers to repairs performed on leaking components without monitoring the component while it is being repaired.

The following descriptions of repair methods include only those features of each fugitive emission source (pump, valve, etc.) which need to be considered in assessing the applicability and effectiveness of each method. They are not intended to be complete repair procedures.

Pumps

Many process units have spare pumps which can be used while repairing the faulty pump. The unit can be isolated without major process disruption while the leaking pump is being repaired. Leaks from packed seals may be reduced by tightening the packing gland. However, at some point, the packing may deteriorate so much that further tightening would have no effect, or would possibly even increase fugitive emissions from the seal. If such is the case, the packing would be replaced with the pump out of service. When mechanical seals are used, the pump must be dismantled so that the leaking seal can be repaired or replaced. Dismantling a pump may result in spills of some process fluid, causing VOC emissions. These temporary emissions could be greater than the continued leak from the seal. Therefore, the pump should be flushed of as much VOCs as possible before opening it to replace the seal.

Compressors

Leaks from packed seals may be reduced by the same repair procedure that was described for pumps. Leaks from other types of seals require that the compressor be out of service for repair. Since extra compressors are not usually kept on-site, repair or replacement of the seal would require a shutdown of the process. If the leak is small, temporary emissions resulting from a shutdown could be greater than if the seal were allowed to leak until the next scheduled shutdown and then repaired.

Pressure Relief Devices

In general, leaking relief valves must be removed for repair. However, if a relief valve has only reseated improperly, manually releasing it may improve its seat. If this is not effective, the valve may need repair or replacement. In order to remove the relief valve without shutting down the process, a block valve is installed upstream of the relief valve. (In some chemical plants, installation of a block valve upstream of a pressure relief device may be a common practice. In other companies, this practice may be forbidden by the operating or

safety procedures of that company, even though allowed by ASME codes.) A spare relief valve should be attached while the faulty valve is repaired and tested. Even though a relief valve has just been repaired or replaced, it is still possible that the next over-pressure relief will result in another leak.

Valves

Most valves have a packing gland that can be tightened while the valve is in service. This procedure should decrease the emissions from the valve. In some cases, however, the emission rate may actually increase if the packing is old and brittle or if the packing gland has been overtightened. Plug-type valves may also be repaired while in service. They can be lubricated with grease to reduce emissions around the plug.

Some valves cannot be repaired while in service and must be isolated from the process and removed for repair or replacement. In some situations, isolating a valve may be relatively easy; for instance, if a manual by-pass loop is available, or if the process operation can be temporarily changed. However, in most cases, isolation of a valve can be achieved only by a process shutdown—a major operation. Also, shutting down a process to isolate a leak may result in more emissions than if the valve were allowed to leak until the next scheduled shutdown and then repaired at that time.

Depending on site-specific factors, it may be possible to repair process valves by injecting a sealing fluid into the source. Injection of sealing fluid has been successfully used to repair leaks from certain valves in petroleum refineries in California.

Open-ended valves allow fugitive emissions to escape through the valve seat. Open-ended valves include drain, purge, sample, and vent valves. Fugitive emissions from open-ended valves can be controlled by installing a cap, plug, flange, or second valve to the open end of the valve. In the case of a second valve, the upstream valve should always be closed after using the valves. Each time the cap, plug, flange, or second valve is opened, any VOC which has leaked through the first valve's seat will be released. These emissions have not been quantified. Control efficiency will depend on the frequency of cap or plug removal. Caps, plugs, etc. for open-ended valves do not affect emissions which may occur during valve use. These emissions may be caused by line purging for sampling, draining, or venting through the open-ended valve.

Flanges

Flange leaks can occasionally be sealed effectively by simply tightening the flange bolts. For a flange leak that requires off-line gasket seal replacement, a total or partial shutdown of the unit would probably be required because most flanges cannot be isolated. For many of these cases, temporary flange repair methods can be used. Unless a leak is major and cannot be temporarily corrected, the emissions resulting from shutting down the unit would probably be larger than the continuous emissions that would result from not shutting down the unit until time for a shutdown for other reasons. Flange leak incidences are very low and many can be corrected by on-line maintenance.

Review Exercise

1. True or False? A leaking mechanical seal requires that the pump be dismantled before it can be repaired.	
2. Generally, most valves can be repaired on-line by tightening the _____.	1. True
3. True or False? Repairing compressor seal leaks is usually no problem, since most plants have many spare compressors.	2. packing gland
4. True or False? In spite of the large number of flanges present, total plant emissions from flanges are generally very small since most flanges have very low leak rates.	3. False
5. _____ maintenance refers to maintenance performed while simultaneously monitoring the leaking component to assess the effectiveness of the repair effort.	4. True
6. If two valves are used, the _____ valve must always be closed first to prevent trapping fluid between the two valves. a. upstream b. downstream	5. a. Directed
7. Leaks from a _____ seal on a pump may be reduced by tightening the _____ gland.	6. a. upstream
	7. packed packing

Structure of Regulations for Leak Detection and Repair

As described in Lesson 2, there are seven industries that currently have or anticipate standards to regulate fugitive emissions of VOCs. In developing fugitive VOC emission standards, each industry was studied separately and a unique set of standards proposed for

that industry. Many of the regulations are very similar. The following factors were addressed for each industry since they determine the effectiveness of a leak detection and repair program:

- action level (definition of a leak)
- applicability (process equipment to be regulated)
- inspection interval (monitoring frequency)
- interval between detection and repair.

The following is a general discussion of how the above factors were used to develop fugitive VOC regulations. No attempt is made to detail all the requirements for each of the industries.

Action Level

The action level is the VOC concentration, observed during monitoring, that defines a leaking component that requires repair. A leak definition can be based on either a concentration value or a "no detectable emission" standard. The "no detectable emission" standard is applied to sources designed to operate in a leakless manner, such as pressure-relief devices with rupture disks or sealless pumps.

The concentration-based value most often used to define a leak is a concentration equal to or greater than 10,000 ppmv. This concentration value is based on the ability to locate leaks in this concentration range and then repair the leak (bring the concentration below 10,000 ppmv). The "no detectable emission" standard is not an absolute zero reading. A violation of the "no detectable emission" limit is defined in Reference Method 21 as "a concentration greater than five percent of the concentration-based leak definition". For example, based on the 10,000 ppmv definition of a leak, a concentration greater than 500 ppmv would be in violation of the "no detectable emission" standard.

Applicability and Inspection Interval

Fugitive emission regulations are generally applicable to specific process components (pumps, compressors, valves, sampling connections, pressure relief devices, and open-ended lines) that are in VOC service. *In VOC service* includes any fugitive emission source that contains or contacts a fluid composed of equal to or greater than 10% VOC by weight. For the benzene fugitive emission regulation, *in benzene service* includes any source that contains or contacts a fluid equal to or greater than 10% benzene by weight.

VOC service can further be divided into light liquid or heavy liquid service. *Light liquid* VOC service is defined as one or more of the stream components having a vapor pressure greater than 0.3 kPa (0.04 psia) at 20 °C (68 °F). All VOC sources with a stream component vapor pressure equal to or less than 0.3 kPa at 20 °C are in *heavy liquid* service. The NSPS for "Refinery Leaks" defines heavy liquid as kerosene or a heavier liquid.

The inspection interval or length of time between monitoring is based on the leak rate and leak frequency of a specific process component and on service conditions. Different intervals are often specified for different process components. For example, the *Draft NSPS for Petroleum Refineries* proposes that most valves in gas or light liquid service, and pumps in light liquid service, be monitored monthly. However, if a diaphragm or bellows valve is used, the valve needs only annual monitoring to demonstrate "no detectable emissions".

It should be noted that certain control equipment can be substituted for periodic leak detection and repair procedures. From the above example, if the pump in light liquid service was equipped with dual mechanical seals and a pressure indicator on the barrier fluid system, then that pump could be exempted from the monthly inspection requirement.

In addition, since valves constitute a large percentage of the components to be monitored (about 90%), alternatives to a periodic inspection cycle have been used to reduce cost. If the owner/operator can prove that the valves achieve a *good performance level* then one or more of the next inspection cycles may be skipped. A good performance level is based on having a low percentage (usually 2%) of valves that are found to leak.

Allowable Interval before Repair

The allowable time before repair reflects a balance between eliminating a source of VOC emissions and allowing the plant operator sufficient time to obtain necessary repair parts and maintain some degree of flexibility in overall plant maintenance scheduling. The *allowable interval before repair* is usually specified as 15 days unless a process shutdown is required. In most cases, the plant operator is required to document when the repairs are first attempted, reasons for any delay in repair (more than 15 days), and when the leaking component was successfully repaired.

Review Exercise

1. The VOC concentration, observed during monitoring, that defines a leaking component that requires repair is referred to as the a. screen. b. action level. c. concentration. d. effort level.	
2. True or False? "No detectable emission" is defined in Reference Method 21 as a concentration equal to zero.	1. b. action level.
3. All process components must be monitored a. weekly. b. monthly. c. annually. d. at varying times, depending upon specific regulations.	2. False
	3. d. at varying times, depending on specific regulations.

4. *In VOC service* is defined as any source that contains or contacts a fluid composed of _____ or more VOCs by weight. a. 10% b. 1% c. 95% d. 0.1%	
5. True or False? All components that are found to leak must be repaired within 1 hour.	4. 10%
6. A _____ VOC service is defined as one or more of the stream components having a vapor pressure greater than 0.3 kPa (0.04 psia) at 20°C (68°F). a. light liquid b. heavy liquid c. mixed liquid	5. False. The component must be repaired as soon as possible, taking into consideration plant maintenance schedules.
	6. a. light liquid

Sources

The text in this lesson was primarily adapted from the following EPA documents.

Draft. Environmental Protection Agency (EPA). August 1981. *Control of Volatile Organic Compound Fugitive Emissions from Synthetic Organic Chemical, Polymer and Resin Manufacturing*. Control Technology Guideline (CTG).

Draft. Environmental Protection Agency (EPA). April 1981. *VOC Fugitive Emissions in Petroleum Refining Industry—Background Information for Proposed Standards*.

Environmental Protection Agency (EPA). July 1980. Assessment of Atmospheric Emissions from Petroleum Refining: Volume 4. Appendix E: Control Technology Review and Evaluation. EPA 600/2-80-075D.

Environmental Protection Agency (EPA). December 1980. Organic Chemical Manufacturing: *Volume 3. Storage, Fugitive and Secondary Sources*. EPA 450/3-80-25.

Lesson 5

Portable VOC Detection Devices

Lesson Goal and Objectives

Goal

To familiarize you with three portable VOC detection devices.

Objectives

Upon completing this lesson, you should be able to:

1. describe the operating principles of three portable VOC detection devices.
2. determine if a portable VOC detector meets the appropriate performance criteria and equipment specifications using EPA Reference Method 21.
3. recognize the appropriate safety procedures.

Introduction

A number of portable VOC detection devices are capable of measuring leaks from process equipment. These devices operate on a variety of principles, the three most common being ionization, infrared absorption, and combustion. Any analyzer can be used, providing that it meets the specifications and performance criteria contained in EPA Reference Method 21.

This lesson is divided into three sections. The first section is a brief description of the operating principles and some of the limitations of portable VOC detection devices. The second section covers the performance criteria required by Reference Method 21. The last section is a brief discussion of safety considerations. A glossary provided at the end of the lesson lists some useful terms used to describe the operation and the capabilities of monitors. Appendix C is a table listing the manufacturers most likely to offer portable VOC detectors. This table also gives the weight, cost, and operating range of these devices.

Operating Principles

Ionization

Ionization refers to the act of forming charged atoms (ions) from a neutral compound. Ionization detectors operate by supplying energy to the sample to ionize it and then measuring the charge (number of ions) produced. Two methods of ionization currently in use are *flame* and *photometric*.

Flame Ionization Detector (FID)

In a flame ionization detector (FID), the sample is injected into a detection chamber where it is exposed to a hydrogen flame. The flame is surrounded by negative collecting electrodes. When most organic vapors burn, they form positively-charged carbon ions as intermediate products of combustion. As these positively charged ions are collected, a calibrated output current is read on a panel meter or recorder (see Figure 5-1).

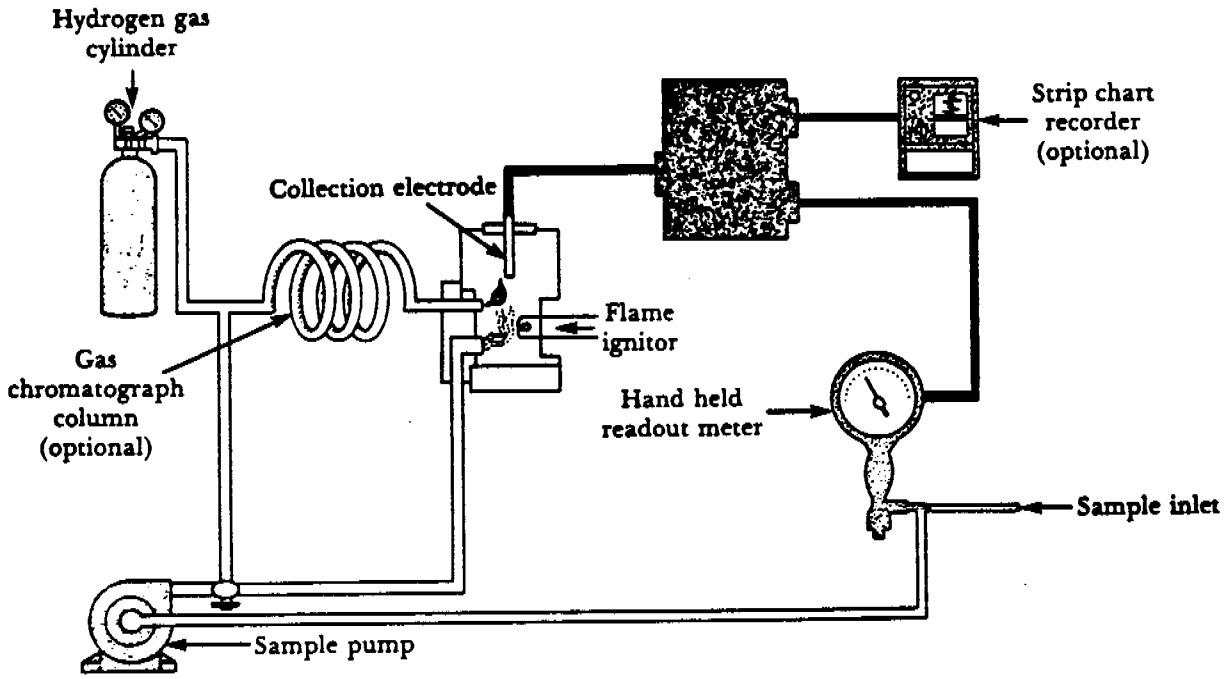


Figure 5-1. Organic vapor detector using flame ionization detector (FID).

Pure hydrogen burning in air (O_2 and N_2) produces very little ionization, so background effects are minimal. Although carbon monoxide and carbon dioxide do not produce interferences, FIDs show a very low sensitivity to water vapor. Additionally, if water condenses in the sample tube, it may block the tube and give erratic readings. As with most gas samplers, a filter is used to remove any particulate matter which may be present.

A standard FID usually measures the total carbon content of the organic vapor sampled. The FID analyzers are calibrated using a calibration gas (such as methane or hexane) and the output is read in parts per million by volume (ppmv) of carbon measured as methane or hexane. With special options, the FID is capable of measuring *total gaseous nonmethane organics* (TGNMO) or individual organic components. TGNMO can be measured by obtaining a reading of the total carbon content in the sample. Then, a carbon filter that will absorb all the organics, except methane, is placed on the detector. Then a second reading is obtained. By subtracting the second value (methane) from the first (total carbon), the TGNMO is obtained. Concentrations of individual organic compounds in a mixture can be measured by the addition of a gas chromatograph.

Certain organic compounds that contain nitrogen, oxygen, or halogen atoms give a reduced response. In addition, some organics may not give any response at all. Also, FIDs manufactured by different companies may respond differently to the same chemical compound. Reference Method 21 requires that a response factor be determined for each compound that is to be measured. These response factors are discussed later. Presently, FIDs are one of the most accepted and widely used detectors for measuring organic leaks from process equipment.

Photo-ionization Detector

Photo-ionization uses ultraviolet light (instead of a flame) to ionize the organic vapors. The detector consists of an argon-filled, ultraviolet (UV) light source that emits photons. A chamber adjacent to this UV light source contains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions that are formed to the collector (negative) electrode. Again, the output current (which is proportional to ion concentration) is read on a meter or recorder.

Presently, only two portable photo-ionization VOC detectors are being marketed. As with FIDs, detector response varies with the functional group in the organic compounds. Photo-ionization detectors have been used to detect leaks in the synthetic organic chemicals industry, especially for certain compounds, (for example, formaldehyde) that will not give a response on an FID or on a combustible detector.

Nondispersive Infrared Detector

Nondispersive infrared (NDIR) spectrometry is a technique based upon the broadband light absorption characteristics of certain gases. Infrared radiation is typically directed through two separate absorption cells—a reference cell and a sample cell. The sealed reference cell is filled with nonabsorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of the gas being analyzed. When a specific hydrocarbon is present, the IR absorption is proportional to the molecular concentration of that gas. The detector consists of a double chamber separated by an impermeable diaphragm. Radiant energy passing through the two absorption cells heats the two portions of the detector chamber differentially. The pressure difference causes the diaphragm between the cells to distend and to vary the capacitance. The variation in capacitance is proportional to the concentration of the component of gas present and is measured electronically.

The NDIR instruments are usually subject to interference, because other gases (e.g., H_2O and CO_2) absorb light at the wavelength of the gas of interest. Efforts to eliminate the interferences by use of reference cells or optical filters are only partially successful. For hydrocarbon monitoring, the detector is filled with one of several different hydrocarbons, such as hexane or heptane, which may be different from the hydrocarbons contained in the sample; this causes a disproportionate response. Therefore, these detectors are generally used only for the detection and measurement of single components.

For these cases the wavelength at which a certain compound absorbs infrared radiation is predetermined, and the device is preset (by the use of optical filters) for that specific wavelength. If set to a wavelength of 3.4 micrometers, infrared devices can be used to

detect and measure petroleum fractions, including gasoline and naphtha, which are known to be mixtures of aliphatic (saturated and unsaturated) and aromatic hydrocarbons.

Combustion Analyzers

Combustion analyzers are designed using one of two principles:

1. by measuring the thermal conductivity of a gas.
2. by measuring the heat produced by combusting the gas.

By far, the most common method used in portable VOC detection devices is measuring the heat of combustion. These devices are referred to as *hot wire detectors* or *catalytic oxidizers*.

One hot wire detector uses a combustion cell composed of two resistance elements. One element is a catalytic-coated filament, the other is uncoated. The combustible gas sample is catalytically oxidized by the coated resistance filament. The resulting heat release changes the filament's resistance. This resistance is then compared to a reference element as shown in Figure 5-2. The resistance value of the reference element is unaltered by the oxidation of combustible gas. The resulting imbalance is easily measured and related to VOC concentration.

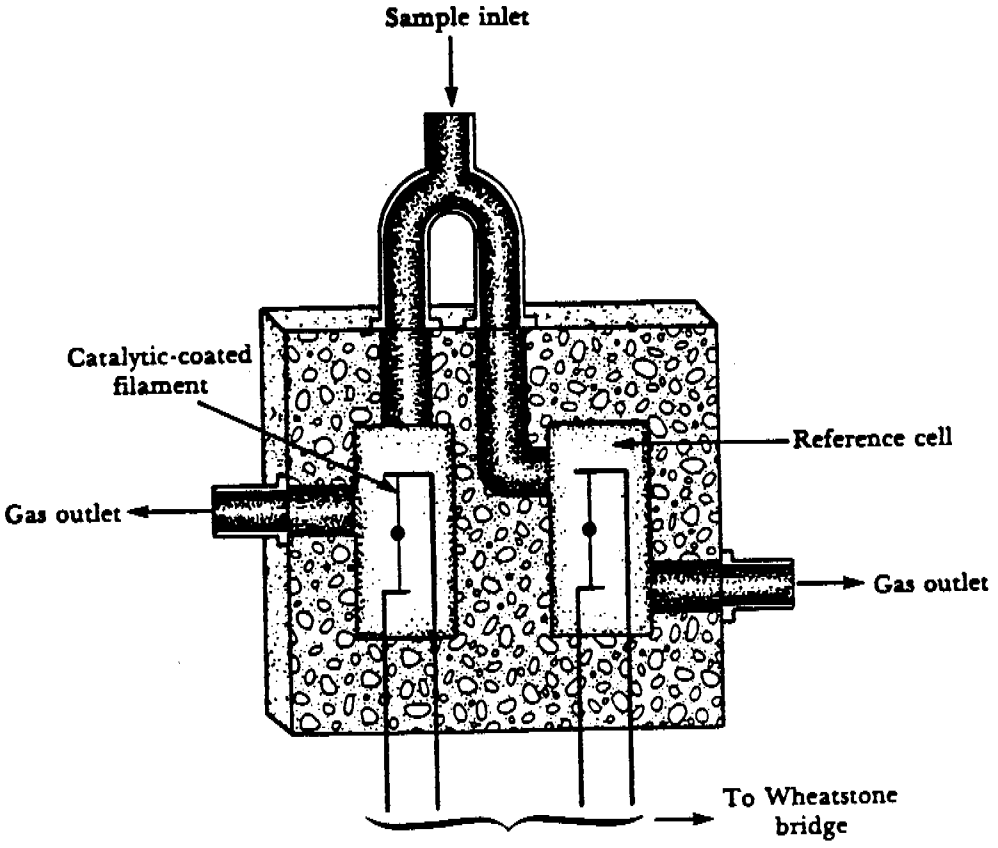


Figure 5-2. Hot wire detector.

Combustion analyzers, like most other detectors, are nonspecific for mixtures of gases. Mixtures must be separated (usually by a chromatographic column) to identify an individual concentration. Although not required by the regulations, identifying an individual concentration may be desirable. In addition, combustion analyzers will give a reduced response to or not detect any gases that are not readily combusted (for example, formaldehyde and carbon tetrachloride). Because of their ease of operation and applicability to most sources, combustion analyzers are widely used in both refineries and SOCMI plants to detect leaks.

Review Exercise

1. FID refers to a _____.

2. True or False? An FID uses a hydrogen flame to combust the sample gas and produce carbon ions that can be easily measured.

3. True or False? Two types of portable *ionization* detectors used to detect leaking process equipment are photo-ionization detectors and infrared detectors.

4. What does the hot wire combustion analyzer measure that is easily related to the concentration of the gas sample?
   a. vapor pressure of the gas sample
   b. partial pressure of the gas sample
   c. heat produced by combustion of the gas sample
   d. latent heat of the gas sample

5. Any portable detection device that meets the specifications and performance criteria of _____ can be used to monitor leaks from process equipment.

1. flame ionization detector

2. True

3. False

4. c. heat produced by combustion of the gas sample

5. Federal Reference Method 21

Performance Criteria and Evaluation Procedures for Portable VOC Detectors

As previously stated, any portable VOC detector may be used as long as it meets the performance criteria specified in Reference Method 21. Reference Method 21 is reproduced in Appendix A. A discussion of the performance criteria and detector evaluation procedure is presented below and summarized in Table 5-1.

Table 5-1. Performance criteria for portable VOC detectors.

Criteria	Requirement	Time interval
Response factor	Must be < 10	One time, before detector is put in service
Response time	Must be ≤ 30 seconds	One time, before detector is put in service. If modification to sample pumping or flow configuration is made, a new test is required.
Calibration precision	Must be $\leq 10\%$ of calibration gas value	Before detector is put in service and at 3-month intervals or next use, whichever is later.

In addition to the performance criteria, Reference Method 21 also requires that the analyzer meet the following specifications:

- the VOC detector shall respond to those organic compounds processed at the plant (determined by the response factor).
- the analyzer shall be capable of measuring the leak definition specified in the regulation (i.e., 10,000 ppmv or "no detectable limit").
- the scale of the analyzer shall be readable to $\pm 5\%$ of the specified leak definition concentration.
- the analyzer shall be equipped with a pump so that a continuous sample is provided at a nominal flow rate of between 0.5 and 3 liters per minute.
- the analyzer shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable standards.

Also, criteria for the calibration gases to be used are specified. Two calibration gases are required for both monitoring and analyzer performance evaluation. One is a zero gas which is air with less than 10 ppmv VOC. The other calibration gas uses a reference compound/air mixture. This calibration gas is also referred to as the reference gas. The concentration of the reference gas is approximately equal to the leak definition. The leak definition and the reference compound are both specified in the applicable regulations. Calibration may be performed using a compound other than the reference compound if a conversion factor is determined for the alternate compound. The resulting meter readings during source surveys can be converted to reference compound results. Often, manufacturers list conversion factors for other gases in their operator's manuals. Because of nonlinear responses, however, care must be taken to use the conversion factor at the action level.

Response Factor

The sensitivity of an analyzer varies, depending on the composition of the sample and concentration detected. The response factor (RF) helps to quantify the sensitivity for each compound. The response factor is defined by:

$$\text{Response factor} = \frac{\text{Actual concentration of compound}}{\text{Observed concentration from detector}}$$

A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The analyzer response factor for individual compounds to be measured must be less than 10.0. The response factor tests are required before placing the analyzer in service, but do not have to be repeated at subsequent intervals.

Response factors can be determined by the following method. First the analyzer is calibrated using the reference gas. Then, for each organic species that is to be measured, a known standard in air is obtained or prepared. The standard should be at a concentration of approximately 80% of the leak definition unless limited by volatility or explosivity. In these cases, a standard at either 90% of the saturation concentration or 70% of the lower explosive limit (LEL) is prepared. This mixture is then injected into the analyzer and the observed meter reading is recorded. The analyzer is then zeroed by injecting zero air until a stable reading is obtained. The procedure is repeated by alternating between the mixture and zero air until a total of three measurements is obtained. A response factor is calculated for each repetition and then averaged over the three runs.

Alternately, if response factors have been published for the compounds of interest for the type of detector, the response factor determination is not required, and existing results may be referenced. Results of a study developing response factors for FID (Foxboro OVA-108 and OVA-128) and catalytic oxidation (J. W. Bacharach TLV Sniffer) analyzers are presented in Appendix B. The values are only for pure organic chemicals.

It is important to note that these response factors are used only as a guide to determine a particular analyzer's appropriateness for detecting a given compound. For example, from the data presented in Appendix B, it can be readily seen that in screening for leaks from a source containing cumene, an FID can be used (RF = 1.87); while the catalytic oxidation detector cannot (RF has no value). Similarly, from the same data, neither of these devices would be capable of detecting leaks from a source containing carbon tetrachloride.

The concept of using response factors as a general guide to analyzer applicability is especially important when dealing with chemical mixtures. Since many process streams in industrial plants are composed of a mixture of chemicals, having a simple method to determine the response factor for a given detector type is important. One EPA study has concluded that analyzer response factors for a mixture fall between the responses expected for the pure components. Therefore, if desired, an interpolated or weighted average can be used to predict the response for mixtures based on known responses for individual chemicals. For further information see EPA 600/2-81-110, *Response of Portable VOC Analyzers to Chemical Mixtures.*

Response Time

The response time of an analyzer is defined as the time interval from a step change in VOC concentration at the input of a sampling system to the time at which 90% of the corresponding final value is reached as displayed on the analyzer readout meter. The response time must be equal to or less than 30 seconds. The response time must be determined for the analyzer configuration that will be used during testing. The response time test is required before placing an analyzer in service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

The response time of an analyzer is determined by first introducing zero gas into the sample probe. When the meter has stabilized, the system is quickly switched to the specified calibration gas. The time, from the switching to when 90% of the final stable reading is reached, is noted and recorded. This test sequence must be performed three times. The reported response time is the average of the three tests.

Calibration Precision

Calibration precision is the degree of agreement between measurements of the same known value. To ensure that the readings obtained are repeatable, a calibration precision test must be completed before placing the analyzer in service, and at 3-month intervals, or at the next use, whichever is later. The calibration precision must be equal to or less than 10% of the calibration gas value.

To perform the calibration precision test, a total of three test runs are required. Measurements are made by first introducing zero gas and adjusting the analyzer to zero. The specified calibration gas (reference) is then introduced and the meter reading is recorded. The average algebraic difference between the meter readings and the known value of the calibration gas is then computed. This average difference is then divided by the known calibration value and multiplied by 100 to express the resulting calibration precision as percent.

Safety

Portable instruments to detect fugitive VOC emissions from stationary sources are required to be used in hazardous locations such as petroleum refineries and bulk gasoline terminals. The National Electrical Code requires that instruments to be used in hazardous locations be certified to be explosion proof, intrinsically safe, or purged.

Hazardous locations are divided into three classes: Class I, Class II, and Class III. Each class is divided into two divisions (Division 1 or 2) according to the probability that a hazardous atmosphere will be present; and also into seven groups depending upon the type of hazardous material exposure. Groups A through D are flammable gases or vapors, and Groups E, F, and G apply to combustible or conducting dusts. Class I, Division 1, Groups A, B, C, and D locations are those in which hazardous concentrations of flammable gases or vapors may exist under normal operating conditions. Class I, Division 2, Groups A, B, C, and D locations are those in which hazardous concentrations of flammables may exist only under unlikely conditions of operation.

Only five manufacturers presently produce certified portable VOC detection instruments. Table 5-2 lists these manufacturers, approved instrument model numbers, and instrument certification categories.

Table 5-2. Portable VOC detection instrument certification.

Manufacturer	Model no.	Certification
Bacharach Instrument Co., Santa Clara, California	L	Intrinsically safe, Class I, Division 1, Groups C and D
	TLV Sniffer	Intrinsically safe, Class I, Division 1, Groups C and D, and Class I, Division 2, Groups A and B
Foxboro, Norwalk, Conneticut	OVA-128	Intrinsically safe, Class I, Division 1, Groups A, B, C, and D
	OVA-108	Intrinsically safe, Class I, Division 1, Groups A, B, C, and D
HNU Systems, Inc. Newton Upper Falls, Massachusetts	PI-101	Intrinsically safe, Class I, Division 2, Groups A, B, C, and D
Mine Safety Appliances Co., Pittsburgh, Pennsylvania	40	Intrinsically safe, Class I, Division 1, Group D, and Class I, Division 2, Groups A, B, and C
Survey and Analysis, Inc., Northboro, Massachusetts	OnMark Model 5	Intrinsically safe, Class I, Division 1, Groups A, B, C, and D

In addition to instrument certification, certain operating procedures and safety precautions must be observed when any portable VOC detection device is used. The very first thing that must be done is to read the operating and service manual very carefully before using the device in the field. Also, to maintain the intrinsic safety which is built into certain detectors, it is imperative that the operating and service manual be consulted before trouble-shooting or servicing.

Flame ionization hydrocarbon detectors are potentially hazardous since they burn hydrogen in the detector cell. Mixtures of hydrogen and air are flammable over a very wide range of concentrations. Therefore, additional safety precautions should be taken when igniting the flame and refilling the hydrogen supply tank. Both these tasks should be carried out in a safe area to ensure that there are no sources of ignition. As can be seen from Table 5-2, one FID analyzer, Foxboro's OVA, has been certified intrinsically safe for use in hazardous atmospheres. Additional safety considerations on field use of these analyzers are discussed in the next lesson, **Inspection Procedures.**

Review Exercise

1. True or False? Reference Method 21 lists the model numbers of the EPA-approved portable VOC detection devices.	
2. The _____ gives a quantitative measure of an analyzer's sensitivity. a. response factor b. precision test c. lag time d. reference gas	1. False
3. True or False? Response factors can be obtained only from the manufacturers of the portable analyzers.	2. a. response factor
4. The reference gas used to calibrate the analyzers is specified a. in Reference Method 21. b. by the manufacturer. c. in the applicable regulation for each source category. d. by the National Bureau of Standards.	3. False
5. True or False? The response time of a specific analyzer partially depends upon its sample flow configuration.	4. c. in the applicable regulation for each source category.
6. True or False? A calibration precision test is required to be performed only before placing the analyzer in service for the first time.	5. True
7. A portable VOC analyzer must be readable to ± _____ of the specified leak definition concentration. a. 5% b. 25% c. 50% d. 0.1%	6. False
	7. a. 5%

8. A portable VOC analyzer must be equipped with a _____ to provide a continuous sample flow.	
9. True or False? Reference Method 21 requires that the portable VOC analyzer be intrinsically safe for use in an explosive atmosphere.	8. pump
10. Federal Reference Method 21 requires that the portable VOC detector have a response time equal to or less than a. 1 second. b. 30 seconds. c. 1 minute. d. 5 minutes.	9. True
	10. b. 30 seconds.

Glossary

Accuracy—The difference between the measured value and the true value that has been established by an accepted reference method procedure. In most cases, a value is quoted by the manufacturer.

Ambient Temperature Range—The range of ambient temperature over which the instrument meets stated performance specifications.

Calibration Gas—The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

Calibration Precision—The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration.

Fall Time—The time interval between the initial response and a 90% response (unless otherwise specified) after a step decrease in the inlet concentration. This measurement is usually, but not necessarily, the same as the rise time.

Interference—Any substance causing a deviation of instrument output from the value that would result from the presence of only the pollutant of concern.

Lag Time—The time interval from a step change in the input concentration at the instrument inlet to the first corresponding change in the instrument output.

Lower Detectable Limit—The smallest quantity or concentration of a sample that causes a response equal to twice the noise level. (Not to be confused with sensitivity, which is the minimum detectable change).

Noise—Spontaneous deviation from a mean output not caused by input concentration changes (expressed as a percentage of the full scale).

Range—The lower and upper detectable limits. (The lower limit is usually reported as 0.0 ppm. This is somewhat misleading and should be reported as the true lower detectable limit.)

Reference Compound—The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

Response Factor—The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

Response Time—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% (unless otherwise specified) of the ultimate recorded output. This measurement is the same as the sum of lag time and rise time.

Sensitivity—The smallest change in inlet concentration which can be detected distinguishable from instrument noise for outputs at mid-scale and 80% of full scale. The magnitude of change in inlet concentration required may differ with pollutant concentration and may also be different for positive and negative displacements.

Span Drift—The change over a stated period of time in instrument output of unadjusted continuous operation when the input concentration is a stated value other than zero (expressed as a percentage of the full scale).

Warmup Time—The elapsed time necessary after startup for the instrument to meet stated performance specifications when the instrument has been shut down for at least 24 hours.

Zero Drift—The change over a stated period of time in instrument output of unadjusted continuous operation when the input concentration is zero (expressed as a percentage of the full scale).

Sources

The text in this lesson was adapted primarily from the following documents:

Environmental Protection Agency (EPA). March 1980. *Summary of Available Portable VOC Detection Instruments*. EPA 340/1-80-010.

Environmental Protection Agency (EPA). January 5, 1981. *Proposed Reference Method 21, Determination of Volatile Organic Compound Leaks*. EPA-46, Federal Register No. 2.

References

Bacharach Instruments. October 1981. *Instruction Manual TLV Sniffer.* Pittsburgh, PA.

Foxboro, *Instruction and Service Manual for Model OVA-108.* S. Norwalk, CT.

Environmental Protection Agency (EPA). September 1981. *Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds.* EPA 600/2-81-051.

Environmental Protection Agency (EPA). September 1981. *Response of Portable VOC Analyzers to Chemical Mixtures.* EPA 600/2-81-110.

Lesson 6

Inspection Procedures

Lesson Goal and Objectives

Goal

To prepare you to inspect process components for VOC leaks.

Objectives

Upon completing this lesson, you should be able to:

1. recognize the preparation and equipment needed to perform inspections.
2. be familiar with the recordkeeping requirements specified in the regulations.
3. distinguish between a source survey based on a concentration or "no detectable emission" limit.
4. recognize appropriate safety procedures.

Introduction

General inspection procedures for individual process components such as valves and pump seals are outlined in Reference Method 21. The inspection procedures for the individual process components are identical for all of the source catagories (SOCMI, refineries, etc.). This lesson will review these inspection procedures, noting some of the problems that may occur and the safety precautions to be observed. It is important to note that plant size and complexity will greatly affect inspection procedures. Therefore, this lesson presents several inspection approaches rather than one standard procedure.

Pre-inspection Preparation

Research

Since any inspection requires labor and expense, minimizing the inspection time spent in the plant is important. The inspector should conduct a thorough search of the agency files on the facility to be inspected. This will help determine the types of process units, the number of process units, and the compliance history and trends of this facility. The inspector should be as informed as possible about the operation of these process units and the potential sources of fugitive VOC emissions. The more the inspector knows, the better he or she will be able to communicate with plant personnel.

The inspector must also review the regulations that are applicable to the facility. Regulations about sources to be inspected, action level (leak definition), and inspection interval should be particularly noted. The inspector can then determine the best schedule for plant visits. Because of the large number of sources, it will generally be impossible to inspect all of them at a specific facility at one time (see Appendix D). Most regulations are developed on the basis of a *process unit* being the affected facility. For example, in a refinery, alkylation and isomerization are both process units. Before entering the plant, the inspector should determine the number of process units he or she intends to inspect. This will enable the inspector to prepare survey log sheets for these process units similar to those maintained by plant operators. Figure 6-1 is an example of a survey log sheet for identifying leaking components.

Leak detection and repair survey log

Process unit_____ **Instrument operator**_____

Analyzer_____

Component	Stream composition			Tag number	Date leak located	Date maintenance performed	Component recheck after maintenance	
	Gas	Liquid					Date	Analyzer reading (ppmv)
		Light	Heavy					

Figure 6-1. Example monitoring survey log sheet.

The number of process units that will be inspected is determined by the level of inspection planned. Generally, the inspections are aimed at maintaining a limited number of units in continuous compliance with the regulations. Therefore, the inspector will periodically screen a random sample of process equipment. These process units can be chosen from plant records or previous inspection reports that indicate any problem areas. If this information is not available, the inspector may wish to choose process units that handle gases or light liquids. For example, in a refinery, these process units would be light ends/gas processing, fluid catalytic cracking, alkylation, and isomerization. The inspection may also be aimed at obtaining strict compliance for the entire facility. For large plants (especially refineries), this would require a group of inspectors working for several days.

Notification

The facility management should be contacted before the inspection date unless a surprise inspection is intended. The facility management should be notified of the intent to inspect and the purpose of the inspection. A date and time can then be arranged and the facility management informed to have the appropriate records available at the time of the inspection. Also, the inspector can find out what safety equipment will be required.

Equipment

Inspecting the facility for equipment leaks requires the inspector to have a portable VOC detector. As discussed in Lesson 4, other methods may be used to detect leaking components; however, this lesson will focus on using a portable VOC detector. In choosing and operating a portable VOC detection device, the following must be considered:

1. Does the detector respond to the compounds being processed and have a response factor less than 10? (Lesson 5 and Appendix B)
2. Does the inspector understand how to start up, use, calibrate, shut down, and in the case of an FID, refuel the detector? The inspector may wish to practice these procedures in the lab or office.
3. Does the instrument meet all the specifications required by Reference Method 21? (Lesson 5 and Appendix A)
4. Has the instrument passed calibration precision and response time tests? Has it been rechecked prior to use? (Lesson 5 and Appendix A)
5. Is the instrument operating properly immediately preceding its use in the field? Has it been calibrated, battery checked, etc.? This is not a requirement of Reference Method 21, but helps eliminate delays in the field.
6. Have arrangements been made so that calibration gas (hexane or methane) is at the inspection site? Also, have arrangements for hydrogen cylinders been made if an FID is to be used?

In addition to the portable VOC detection device, the inspector must also carry paper and pencil. An inspection team should consist of at least two persons—one person to operate the portable VOC detector and the other to take the necessary notes.

Review Exercise

1. The EPA reference method for the determination of VOC leaks from process components is a. 5. b. 2. c. 25. d. 21.	
2. Most regulations governing VOC leaks consider the _____ to be the affected facility. a. process unit b. entire plant c. component	1. d. 21.
3. The leak definition is given in a. Reference Method 21. b. the appropriate regulation.	2. a. process unit
4. Specifications and performance criteria for portable VOC detectors are given in a. Reference Method 21. b. the appropriate regulation.	3. b. the appropriate regulation.
5. Before a plant inspection, the inspector must review the applicable regulations for the facility being inspected for a. sources to be inspected. b. action level. c. inspection interval. d. all of the above	4. a. Reference Method 21.
6. To perform Reference Method 21, the inspector is required to use a _____ to locate leaks. a. portable VOC detector b. soap bubble solution with glycol c. transmissometer d. mechanical seal	5. d. all of the above
	6. a. portable VOC detector

General Field Procedures

This section covers a number of important aspects involved in the plant visit and inspection. Because of the number of and different types of source categories, this section will outline general approaches to conducting an inspection, rather than recommend a standard procedure.

Inspection of Plant Records

Any facility affected by VOC fugitive emission regulations will be required to keep records to verify compliance. The specific amount of information required (pertaining to leak detection and repair) varies depending upon the regulations applicable to that particular facility. The regulations should be checked to determine the specific recordkeeping requirements for each facility. Recordkeeping is usually required in three different categories of the control program: leak monitoring; control equipment; and equipment capable of meeting a "no detectable emission" limit. In general, the following information must be kept in the plant log:

1. Leak monitoring
   - Instrument and identification number of any source found to be leaking
   - Date that the leak was detected and dates of each attempt to repair
   - Repair methods applied, expected date of successful repair if it must be delayed (usually by more than 15 days), and the date of successful repair
   - Weatherproof and readily visible tag on leaking source, which will be removed after repair and remonitoring (usually two inspection cycles)
2. Control equipment (refers to closed-vent systems, combustion devices, dual mechanical seals with pressure indicators, and vapor recovery systems)
   - Schematics, design specifications, and piping and instrumentation diagrams of these systems
   - Dates and description of any changes to these systems
   - Dates of any shutdowns or malfunctions
3. Equipment meeting a "no detectable emission" limit
   - A listing with identification numbers of equipment designated as meeting the "no detectable emission" limit
   - Dates of verification test for "no detectable emission" limit
   - Background level and maximum VOC concentration from source measured at each verification test.

Records such as the above are examined to determine compliance, but can also be used as a guide for the inspection to determine the process units to monitor. Two general approaches can be used: chronic leakers can be checked to ensure proper repair; or leak-free units may be monitored to verify the plant data.

Individual Source Surveys

Before each use, the portable VOC detector must be calibrated. The detector is assembled and started according to the manufacturer's instructions. The detector must be allowed to warm up for the appropriate period of time; for example, five minutes for the Century

Systems OVA and ten minutes for the TLV Sniffer. The instrument is then adjusted to zero. (In some cases, zero may be adjusted up-scale to enable the operator to read any negative deflections). Calibration gas is then injected into the analyzer and the meter readout adjusted to the corresponding calibration gas value. If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before using the analyzer.

The definition of what constitutes a leak determines the procedure used in an individual source survey. Definitions of a leak are given in the regulations for each source category and are either based on a concentration (e.g., 10,000 ppmv) or stated as "no detectable emission" limit. The following procedures used to screen process components are taken directly from Reference Method 21.

Leak Definition Based on Concentration

Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately twice the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific pieces of equipment follow (Figures 6-2 and 6-3).

Valves—The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem leaves the packing gland. Sample the stem circumference. Also, place the probe at the interface of the packing-gland-take-up-flange seat and sample the periphery. In addition, survey valve housings of multipart assemblies at the surface of all interfaces where leaks could occur.

Flanges and other connections—For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

Pumps and compressors—Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft seal interface. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leaks could occur.

Pressure relief devices—The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

Process drains—For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a pheripheral traverse.

Open-ended lines or valves—Place the probe inlet at approximately the center of the opening to the atmosphere.

Seal system degassing vents and accumulator vents—Place the probe inlet at approximately the center of the opening to the atmosphere.

Access door seals—Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

Leak Definition Based on "No Detectable Emission"

Determine the background concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of 1 to 2 meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Move the probe inlet to the surface of the source and conduct the same survey described in the preceding section. If an increase greater than 5% of the leak definition concentration is obtained, record and report the results as specified by the regulation.

For those cases where the regulation requires installing a specific device, or ducting or piping specified vents to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that "no detectable emissions" exist, visual observations and sampling surveys are required. Examples of this technique are as follows:

Pump or compressor seals—If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

Seal system degassing vents, accumulator vessel vents, pressure relief devices—If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur in front of the control device. If the required ducting or piping exists, and there are no sources where the emissions could be vented to the atmosphere in front of the control device, then it is presumed that "no detectable emissions" are present.

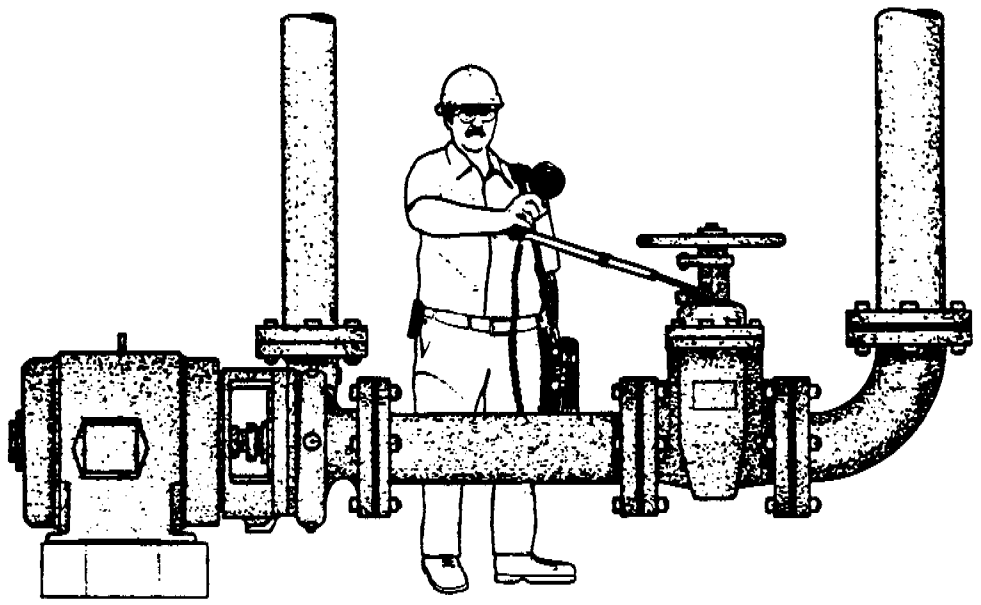


Figure 6-2. Field inspection.

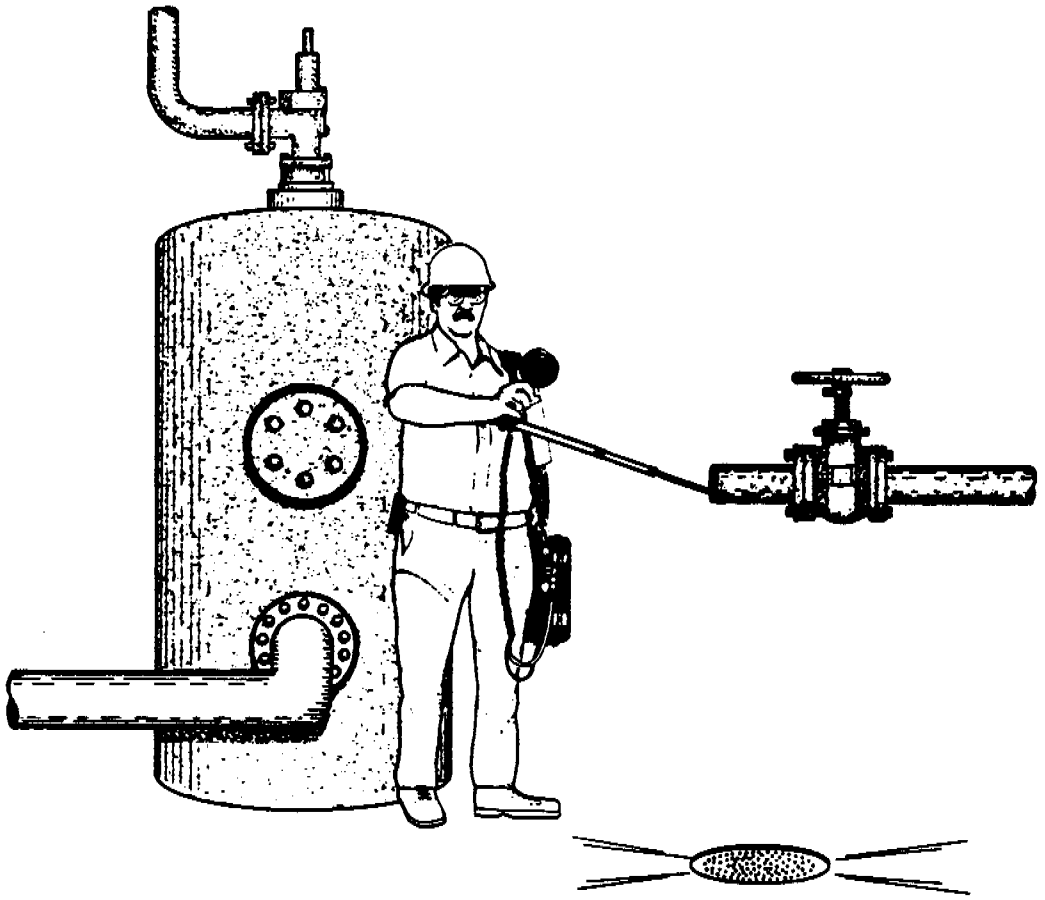


Figure 6-3. Field inspection.

Common Operating Problems

One of the main problems in monitoring organic vapors is locating or pinpointing the leaking source. Organic vapors are dispersed by the wind, sometimes making it difficult to determine their source. It is important that the probe be moved slowly; the slower the instrument response time, the slower the probe must be moved. Placing a notebook or something similar (to block the wind) on the upwind side of the suspected leaking source may help locate the leak, but is not required by Reference Method 21.

In some cases, it may be difficult to determine whether a meter response is caused by high ambient air hydrocarbons or by a source leak, particularly when the ambient reading is highly variable. This problem is commonly experienced in enclosed areas. One method to determine if the source is leaking is to place the probe at the leak source and then remove it from the leak source. This operation is repeated at regular intervals. If the movement of the needle corresponds to the placement and removal of the probe (keeping in mind the analyzer response time), the source is probably leaking. The screening value is then determined by subtracting the ambient reading from the measured screening result. A variety of such situations may be encountered and a judgment on the part of the operator may be required to obtain a representative reading.

Occasionally, a source may be encountered which has a highly variable leak rate. In general the maximum sustained reading or the maximum repeatable reading should be recorded. Again, a judgment on the part of the operator may be required to obtain a representative reading.

A further screening difficulty may arise when screening sources contain heavier hydrocarbon streams, particularly hot sources. When these sources are screened, some of the vapor tends to condense on the internal surfaces of probe-sample hoses. The response of the meter is considerably slower for these sources than for lighter hydrocarbons. And, the meter may require more time to return to zero. When screening heavier hydrocarbons, the meter should be allowed to stabilize before recording the result. The meter should be allowed to return to about 20% of the recorded value. Before screening the next source, sufficient time should be allowed for the meter to stabilize or return to zero. Often the meter will not return completely to zero and a considerable adjustment may be required.

Under no circumstances should the end of the probe be placed in contact with liquid. If liquid is drawn through the sample hose, it may damage the analyzer. A liquid trap, connected between the analyzer and the sample probe, can be used. In addition, equipment components may be covered with a film of grease or dirt If the probe touches these components the grease may plug the probe. The inspector can carry a package of pipe cleaners to clean out the probe, or he/she can use a Teflon extension, and if it gets clogged simply cut off the end.

Safety Considerations

Some components might be considered unsafe to monitor because process conditions include extreme temperatures or pressures. Less frequent monitoring intervals for these components may be required because of the potential danger that may be presented to monitoring personnel. For example, some pumps might be monitored at times when process conditions are such that the pumps are not operating under extreme temperatures or pressures. When using a portable VOC detector, the following safety practices are suggested:

1. Do not place a rigid probe in contact with a moving part such as a rotating pump shaft. A short, flexible probe extension tip may be used.
2. Do not place the umbilical cord from the detector on a heated surface such as a pipe, valve, heat exchanger, or furnace.

Some components may be difficult to reach because they are located in elevated areas. Occasionally these components might be reached by using a ladder or scaffolding. However, extreme caution should be used in attempting to monitor any component which requires that the inspector climb higher than two meters above permanent support surfaces.

Also, it should be mentioned that each plant will have its own safety procedures. These procedures may involve wearing of protective clothing, restrictions on the use of tools in certain areas and contacting the safety officer. Since these procedures are different for each plant it is not the intent of this manual to cover them. However, before inspecting any facility, the plant safety officer should be contacted.

Review Exercise

1. True or False? Equipment that meets a "no detectable emission" limit never has to be monitored for leaks.	
2. True or False? Leaking equipment must be tagged with a weatherproof and readily visible marker until it is repaired and rescreened.	1. False
3. Immediately before each use a portable VOC detector must be a. tested for calibration precision. b. tested for response time. c. used to determine the response factor.	2. True
4. For screening potential leaking components, the probe is placed a. at the surface where leakage could occur. b. 5 cm from where leakage could occur. c. 10 cm from where leakage could occur. d. 25 cm from where leakage could occur.	3. a. tested for calibration precision.
5. When a leak is found, the probe is moved until the maximum meter reading is obtained. The probe is then left at this location for approximately twice the instrument a. response factor. b. response time. c. precision time.	4. a. at the surface where leakage could occur.
6. True or False? For a leak definition based on "no detectable emissions", the ambient concentration near the source must be obtained. This is done by moving the probe upwind and downwind at a distance of at most 1 to 2 meters or no closer than 25 centimeters from the source.	5. b. response time.
7. True or False? When an inspector notices liquid on equipment components, he should place the probe tip in the liquid to determine if it is a VOC.	6. True
	7. False

8. True or False? Some equipment components might be considered unsafe to monitor because process conditions include extreme temperatures or pressures.	
9. One of the main problems in monitoring organic vapors is _____ the leaking source.	8. True
	9. locating (or pinpointing)

Sources

The text for this lesson was adapted primarily from the following EPA documents.

Environmental Protection Agency (EPA). March 1980. *Petroleum Refinery Enforcement Manual.* EPA 340/1-80-008.

Smith, C. D. March 1980. Methodology—Sampling and Analysis of Atmospheric Emissions from Petroleum Refineries in *Proceedings: Symposium on Atmospheric Emissions from Petroleum Refineries* (November 1979, Austin, TX). EPA 600/9-80-013.

Appendix A

Method 21. Determination of Volatile Organic Compound Leaks

1. **Applicability and Principle**

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

2. **Definitions**

2.1 Leak Definition Concentration. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

2.2 Reference Compound. The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. [For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.]

2.3 Calibration Gas. The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

2.4 No Detectable Emission. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is not present. Since background VOC concentrations may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than 5 percent of the leak definition concentration indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

2.5 Response Factor. The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

2.6 Calibration Precision. The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

2.7 Response Time. The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

3.0 Apparatus

3.1 Monitoring Instrument.

3.1.1 Specifications.

a. The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

b. The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

c. The scale of the instrument meter shall be readable to ±5 percent of the specified leak definition concentration.

d. The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be ½ to 3 liters per minute.

e. The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association).

3.1.2 Performance Criteria.

a. The instrument response factors for the individual compounds to be measured must be less than 10.

b. The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

c. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

d. The evaluation procedure for each parameter is given in Section 4.4.

3.1.3 Performance Evaluation Requirements.

a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

3.2 Calibration Gases. The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, <10 ppmv VOC) and a calibration gas in air mixture approx-

imately equal to the leak definition specified in the regulation. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within ± 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternately, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within ± 2 percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results.

4. Procedures

4.1 Pretest Preparations. Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

4.2 Calibration Procedures. Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the appropriate warmup period and zero or internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value. [Note: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.]

4.3 Individual Source Surveys.

4.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

a. Valves—The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where leaks could occur.

b. Flanges and Other Connections—For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

c. Pumps and Compressors—Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

d. Pressure Relief Devices—The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

e. Process Drains—For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

f. Open-Ended Lines or Valves—Place the probe inlet at approximately the center of the opening to the atmosphere.

g. Seal System Degassing Vents and Accumulator Vents—Place the probe inlet at approximately the center of the opening to the atmosphere.

h. Access Door Seals—Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

4.3.2 Type II—"No Detectable Emission".

Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and conduct a survey as described in 4.3.1. If an increase greater than 5 percent of the leak definition concentration is obtained, record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) Pump or Compressor Seals—If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices—If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present.

4.4 Instrument Evaluation Procedures. At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 Response Factor. Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 80 percent of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 90 percent of the saturation concentration, or 70 percent of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a

stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 5.

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

5. Bibliography

5.1 DuBose, D. A., and G. E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-051. September 1981.

5.2 Brown, G. E., et al. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-022. May 1981.

5.3 DuBose, D. A., et al. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-110. September 1981.

Appendix B

Response Factors of VOC Analyzers for Selected Organic Chemicals

This appendix presents the results of a laboratory study on the sensitivity of two portable volatile organic compound (VOC) analyzers to a variety of organic chemicals. The two analyzers tested were the Century Systems OVA-108 and the Bacharach TLV Sniffer.

In Table B-1 are response factors for a 10,000 ppmv meter reading of the instruments along with the 95% confidence intervals. The instruments were calibrated to 7993 ppmv methane gas.

Most of the response factors and associated confidence intervals were calculated using the classical regression method; those computed using the inverse regression method are noted in this table with the explanatory code "I". Other explanatory codes used indicate data availability, date applicability, and possible data uncertainties such as the presence of outliers.

Table B-2 lists compounds tested which do not appear to respond at a 10,000 ppmv reading at any concentration. Questionable or borderline cases were included in Table B-1 rather than Table B-2.

Reference

Environmental Protection Agency (EPA). September 1981. *Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds*. EPA 600/2-81-051. Research Triangle Park, NC.

Table B-1. Response factors with 95% confidence intervals estimated at 10,000 ppmv response.

OCPDB* ID no.	Compound name	Volatility class**	OVA			TLV			
			Response factor		Confidence intervals	Response factor		Confidence intervals	
70	Acetic acid	LL	1.64		1.11, 2.65	15.60		7.05,	46.20
80	Acetic anhydride	LL	1.39		1.09, 1.86	5.88	I	2.71,	12.80
90	Acetone	LL	0.80		0.57, 1.20	1.22		0.81,	2.00
100	Acetone cyanohydrin	HL	3.51		0.69, >100.00	21.00	N	1.09,	>100.00
110	Acetonitrile	LL	0.95		0.85, 1.06	1.18		0.94,	1.52
120	Acetophenone	HL	18.70		5.52, >100.00		B		
125	Acetyl chloride	LL	2.04		1.72, 2.48	2.72		1.65,	5.32
130	Acetylene	G	0.39		0.36, 0.43		B		
150	Acrylic acid	LL	4.59		3.38, 6.57		B		
170	Acrylonitrile	LL	0.97		0.80, 1.20	3.49	I	0.44,	27.90
	Allene	G	0.64		0.60, 0.69	15.00		9.68,	26.50
200	Allyl alcohol	LL	0.96		0.76, 1.27		X		
250	Amyl alcohol, N-	HL	0.75		0.57, 1.04	2.14		0.45,	>100.00
2855	Amylene	LL	0.44		0.34, 0.61	1.03		0.59,	2.59
330	Anisole	LL	0.92		0.65, 1.46	3.91		0.52,	>100.00
360	Benzaldehyde	HL	2.46		1.38, 5.62		B		
380	Benzene	LL	0.29		0.28, 0.31	1.07		0.96,	1.20
450	Benzonitrile	HL	2.99		1.18, 15.30		B		
490	Benzoyl chloride	HL	22.10	D	3.43, >100.00		B		
530	Benzyl chloride	HL	15.30	D	3.96, >100.00		B		
570	Bromobenzene	LL	0.40		0.34, 0.48	1.19		0.27,	>100.00
590	Butadiene, 1,3-	G	0.57		0.54, 0.60	10.90		8.11,	15.40
	Butane, N-	G	0.50		0.46, 0.55	0.63		0.58,	0.70
640	Butanol, N-	LL	1.44	I	0.89, 2.34	4.11	I	2.16,	7.85
650	Butanol, Sec-	LL	0.76		0.70, 0.83	1.25		0.99,	1.66
660	Butanol, Tert-	S	0.53		0.38, 0.81	2.17		1.34,	4.43
592	Butene, 1-	G	0.56		0.51, 0.62	5.84		4.20,	8.89
600	Butyl acetate	LL	0.66		0.54, 0.83	1.38		1.15,	1.70
630	Butyl acrylate, N-	LL	0.70		0.63, 0.78	2.57	I	1.17,	5.68
	Butyl ether, N-	LL	2.60		0.81, 95.60	3.58	I	1.82,	7.04
	Butyl ether, Sec-	LL	0.35		0.21, 0.95	1.15		0.75,	2.17
670	Butylamine, N-	LL	0.69		0.53, 0.98	2.02		1.14,	4.97
680	Butylamine, Sec-	LL	0.70		0.58, 0.87	1.56		0.77,	5.24
690	Butylamine, Tert-	LL	0.63		0.58, 0.70	1.95		1.42,	2.91
	Butylbenzene, Tert-	HL	1.32		0.89, 2.20		B		
750	Butyraldehyde, N-	LL	1.29		1.07, 1.61	2.30		0.96,	12.80
760	Butyric acid	HL	0.80		0.58, 3.14	10.70	I	6.53,	17.60
780	Butyronitrile	LL	0.52		0.40, 0.74	1.47	I	0.62,	3.48
790	Carbon disulfide	LL		B		3.92		1.87,	12.60
830	Chloroacetaldehyde	LL	9.10		5.73, 16.20	5.07		3.08,	9.79
890	Chlorobenzene	LL	0.38		0.32, 0.47	0.88		0.77,	1.00
1740	Chloroethane	G	5.38	I	1.87, 26.40	3.90	P	1.58,	14.10
930	Chloroform	LL	9.28		5.19, 20.00		B		
960	Chlorophenol, O-	HL	4.56		1.72, 27.20	18.50	I	6.50,	51.50
	Chloropropene, 1-	LL	0.67		0.61, 0.73	0.87		0.69,	1.16
210	Chloropropene, 3-	LL	0.80		0.72, 0.90	1.24		1.08,	1.42
970	Chlorotoluene, M-	LL	0.48		0.45, 0.51	0.91		0.40,	7.47
980	Chlorotoluene, O-	LL	0.48		0.42, 0.55	1.06		0.33,	>100.00
990	Chlorotoluene, P-	LL	0.56		0.52, 0.61	1.17	I	0.77,	1.77
1010	Cresol, O-	S	0.96		0.70, 1.45	4.36	I	0.40,	47.40
1040	Crotonaldehyde	LL	1.25		0.82, 2.24		B		
1060	Cumene	LL	1.87		1.10, 3.71		B		
1120	Cyclohexane	LL	0.47		0.39, 0.58	0.70		0.62,	0.80
1130	Cyclohexanol	HL	0.85		0.65, 1.20		B		
1140	Cyclohexanone	LL	1.50		0.97, 2.76	7.04		1.59,	>100.00
1150	Cyclohexene	LL	0.49		0.42, 0.57	2.17		1.78,	2.74
1160	Cyclohexylamine	LL	0.57		0.42, 0.86	1.38		1.28,	1.48
	Decane	HL	0.09	N	0.05, >100.00	0.16	I	0.07,	0.35
1190	Diacetone alcohol	HL	1.45		0.96, 2.48	0.98		0.44,	5.95
	Diacetyl	LL	1.54		1.25, 1.92	3.28		2.25,	5.12
1270	Dichloro-1-propene, 2,3-	LL	0.75		0.56, 1.09	1.75		1.14,	3.18
1215	Dichlorobenzene, M-	HL	0.64		0.55, 0.77	2.36		0.58,	>100.00
1216	Dichlorobenzene, O-	HL	0.68		0.47, 1.11	1.26		0.35,	>100.00
	Dichloroethane, 1,1-	LL	0.78		0.62, 1.02	1.86		1.56,	2.25
1244	Dichloroethane, 1,2-	LL	0.95		0.77, 1.22	2.15		1.66,	2.92

OCPDB* ID no.	Compound name	Volatility class**	OVA				TLV			
			Response factor		Confidence intervals		Response factor		Confidence intervals	
1255	Dichloroethylene, CIS1,2-	LL	1.27		1.05,	1.56	1.65		0.99,	3.47
1256	Dichloroethylene, TRANS 1,2-	LL	1.11		0.98,	1.27	1.66		0.67,	12.60
2620	Dichloromethane	LL	2.81		2.15,	3.87	3.85		2.46,	6.88
3110	Dichloropropane, 1,2-	LL	1.05		0.82,	1.35	1.65		1.06,	3.05
1440	Diisobutylene	LL	0.35		0.29,	0.44	1.41		0.96,	2.40
1870	Dimethoxy ethane, 1,2-	LL	1.22		0.64,	3.61	1.52		0.65,	8.38
1490	Dimethylformamide, N,N-	LL	4.19		2.90,	6.58	5.29		4.05,	7.20
1495	Dimethylhydrazine 1,1-	LL	1.05		0.77,	1.45	2.70		0.51,	>100.00
1520	Dimethylsulfoxide	HL	0.07	I	0.05,	0.11	8.45	I	4.15,	17.20
1480	Dioxane	LL	1.48		1.04,	2.33	1.31		0.70,	3.60
1650	Epichlorohydrin	LL	1.69		1.56,	1.84	2.05		1.79,	2.33
	Ethane	G	0.65		0.44,	1.58	0.69	I	0.21,	2.30
1660	Ethanol	LL	1.78		1.59,	2.01		X		
1910	Ethoxy ethanol, 2-	LL	1.55		1.26,	1.96	1.82		0.96,	5.12
1670	Ethyl acetate	LL	0.86		0.77,	0.95	1.43		1.07,	2.00
1680	Ethyl acetoacetate	HL	3.82		1.89,	10.70	5.60		1.93,	38.80
1690	Ethyl acrylate	LL	0.77		0.63,	0.97		X		
1750	Ethyl chloroacetate	LL	1.99		1.70,	2.36	1.59		0.40,	>100.00
1990	Ethyl ether	LL	0.97		0.77,	1.30	1.14		0.94,	1.42
1710	Ethylbenzene	LL	0.73		0.52,	1.11	4.74	D	1.38,	61.30
1770	Ethylene	G	0.71		0.63,	0.82	1.56		1.26,	2.06
1980	Ethylene oxide	G	2.46		1.95,	3.29	2.40		0.96,	>100.00
1800	Ethylenediamine	LL	1.73		1.29,	2.46	3.26		0.78,	>100.00
2060	Formic acid	LL	14.20		10.60,	19.80		B		
2105	Glycidol	LL	6.88		3.33,	19.70	5.66		2.08,	34.70
	Heptane	LL	0.41	I	0.28,	0.60	0.73		0.33,	6.10
	Hexane, N-	LL	0.41		0.38,	0.45	0.69		0.63,	0.76
	Hexene, 1-	LL	0.49		0.39,	0.66	4.69	D	0.85,	>100.00
	Hydroxyacetone	LL	6.90		4.45,	12.10	15.20		6.11,	66.40
	Isobutane	G	0.41		0.29,	1.04	0.55		0.41,	0.81
2200	Isobutylene	G	3.15		0.90,	38.50		B		
2350	Isoprene	LL	0.59		0.46,	0.80		X		
2360	Isopropanol	LL	0.91		0.72,	1.20	1.39		0.94,	2.31
2370	Isopropyl acetate	LL	0.71		0.62,	0.83	1.31		1.04,	1.72
2390	Isopropyl chloride	LL	0.68		0.60,	0.77	0.98		0.82,	1.22
	Isovaleraldehyde	LL	0.64		0.57,	0.74	2.19	D	1.14,	6.65
2450	Mesityl oxide	LL	1.09		0.94,	1.29	3.14		1.43,	12.00
	Methacrolein	LL	1.20		0.90,	1.71	3.49	D	1.51,	19.80
2460	Methacrylic acid	HL	0.82		0.31,	14.70	1.06	I	0.24,	4.56
2500	Methanol	LL	4.59	P	3.61,	5.60	2.01		1.66,	2.48
1930	Methoxy-ethanol, 2-	LL	2.25		1.62,	3.34	3.13		1.13,	27.40
2510	Methyl acetate	LL	1.74		1.46,	2.13	1.85		1.44,	2.49
	Methyl acetylene	G	0.61		0.58,	0.64	6.79		4.86,	10.40
2560	Methyl chloride	G	1.44		1.22,	1.76	1.84		0.73,	>100.00
2640	Methyl ethyl ketone	LL	0.64		0.51,	0.84	1.12		0.93,	1.38
2645	Methyl formate	LL	3.11		2.42,	4.14	1.94		1.72,	2.21
2665	Methyl methacrylate	LL	0.99		0.90,	1.10	2.42		1.39,	5.38
2650	Methyl-2-pentanol, 4-	LL	1.66		1.27,	2.32	2.00		1.40,	3.15
2660	Methyl-2-pentanone, 4-	LL	0.56		0.46,	0.69	1.63		1.22,	2.35
2550	Methyl-3-buryn-2-OL, 2-	LL	0.59		0.44,	0.86		X		
	Methylal	LL	1.37		1.06,	1.83	1.46		1.24,	1.74
2540	Methylaniline, N-	HL	4.64		3.91,	5.57	9.46		2.55,	35.20
2570	Methylcyclohexane	LL	0.48		0.28,	1.39	0.84		0.68,	1.09
	Methylcyclohexene, 1-	LL	0.44		0.36,	0.54	2.79		1.79,	5.12
2670	Methylpentynol	LL	1.17		0.71,	2.48	3.42		1.83,	8.54
2690	Methylstyrene, A-	LL	15.90		9.50,	21.50		B		
2700	Morpholine	LL	0.92		0.67,	1.40	2.59	I	0.64,	10.50
2770	Nitrobenzene	HL		B			0.01	I	0.00,	82.80
2790	Nitroethane	LL	1.40		1.20,	1.65	3.45		1.56,	15.00
2791	Nitromethane	LL	3.52		3.03,	4.15	7.60		1.91,	>100.00
2795	Nitropropane	LL	1.05		0.80,	1.48	2.02		1.17,	4.47
	Nonane-N	LL	1.54		0.94,	2.98	11.10		3.13,	>100.00
	Octane	LL	1.03		0.89,	1.21	2.11		1.68,	2.75

OCPDB* ID no.	Compound name	Volatility class**	OVA				TLV			
			Response factor		Confidence intervals		Response factor		Confidence intervals	
2851	Pentane	LL	0.52		0.42,	0.66	0.63		0.57,	0.70
2973	Picoline, 2-	LL	0.43		0.38,	0.50	1.18		1.08,	1.29
	Propane	G	0.55	I	0.46,	0.72	0.60	P	0.59,	0.69
3063	Propionaldehyde	LL	1.14		1.00,	1.32	1.71		1.11,	3.06
3066	Propionic acid	LL	1.30		1.03,	1.70	5.08	D	0.73,	>100.00
3070	Propyl alcohol	LL	0.93		0.77,	1.16	1.74		1.06,	3.50
	Propylbenzene, N-	LL	0.51		0.45,	0.58		B		
3090	Propylene	G	0.77		0.44,	2.66	1.74	I	0.15,	20.30
3120	Propylene oxide	LL	0.83		0.74,	0.95	1.15		0.69,	2.46
3130	Pyridine	LL	0.47		0.40,	0.55	1.16		1.03,	1.34
3230	Styrene	LI	4.22		3.45,	5.27		B		
3290	Tetrachloroethane, 1,1,1,2-	LL	4.83	D	1.24,	>100.00	6.91		3.14,	22.50
3291	Tetrachloroethane, 1,1,2,2-	LL	7.89		5.01,	13.80	25.40		8.06,	>100.00
2860	Tetrachloroethylene	LL	2.97		1.71,	6.11		B		
3349	Toluene	LL	0.39		0.36,	0.43	2.68	D	0.79,	>100.00
3393	Trichlorobenzene, 1,2,4-	HL	1.21	I	0.50,	2.94	0.47	I	0.32,	0.68
3395	Trichloroethane, 1,1,1-	LL	0.80		0.72,	0.90	2.40		1.81,	3.35
3400	Trichloroethane, 1,1,2-	LL	1.25		1.05,	1.50	3.69		2.77,	5.16
3410	Trichloroethylene	LL	0.95		0.83,	1.09	3.93		2.68,	6.32
3420	Trichloropropane, 1,2,3-	LL	0.96		0.64,	1.78	1.99		1.27,	3.82
3450	Triethylamine	LL	0.51		0.40,	0.70	1.48		0.96,	2.76
3510	Vinyl acetate	LL	1.27		0.95,	1.82	5.91	D	1.26,	>100.00
3520	Vinyl chloride	G	0.84		0.61,	1.38	1.06		0.59,	4.60
	Vinyl propionate	LL	1.00	I	0.57,	1.74	1.21	I	0.46,	3.20
3530	Vinylidene chloride	LL	1.12		0.87,	1.52	2.41		1.82,	3.35
3570	Xylene, P-	LL	2.12		1.71,	2.68	7.87		3.49,	24.90
3550	Xylene, M-	LL	0.40		0.36,	0.46	5.87	D	0.91,	>100.00
3560	Xylene, O-	LL	0.43		0.28,	0.85	1.40		0.61,	9.33

*Organic Chemical Producers Data Base
**G = gas; LL = light liquid; HL = heavy liquid

Definition of explanatory data codes:

I = inverse estimation method
D = possible outliers in data
N = narrow range of data
X = no data available
B = 10,000 ppmv response unachievable
P = suspect points eliminated

Table B-2. Tested compounds which appear to be unable to achieve an instrument response of 10,000 ppmv at any feasible concentration.

OVA		TLV	
OCPDB*	Compound name	OCPDB	Compound name
—	Acetyl-1-propanol, 3-	120	Acetophenone
790	Carbon disulfide	—	Acetyl-1-propanol, 3-
810	Carbon tetrachloride	130	Acetylene
—	Dichloro-1-propanol, 2,3-	160	Acrylic acid
—	Dichloro-2-propanol, 1,3-	360	Benzaldehyde
—	Diisopropyl benzene, 1,3-	450	Benzonitrile
—	Dimethylstyrene, 2,4-	490	Benzoyl chloride
1221	Freon 12	530	Benzyl chloride
2073	Furfural	—	Butylbenzene, Tert-
—	Methyl-2,4-pentanediol, 2-	810	Carbon tetrachloride
1660	Monoethanolamine	930	Chloroform
2770	Nitrobenzene	1040	Crotonaldehyde
2910	Phenol	1060	Cumene
—	Phenyl-2-propanol, 2-	1130	Cyclohexanol
		—	Dichloro-1-propanol, 2,3-
		—	Dichloro-2-propanol, 1,3-
		—	Diisopropyl benzene, 1,3-
		—	Dimethylstyrene, 2,4-
		2060	Formic acid
		1221	Freon 12
		2073	Furfural
		2200	Isobutylene
		—	Methyl-2,4-pentanediol
		2690	Methylstyrene, A-
		1660	Monoethanolamine
		2910	Phenol
		—	Phenyl-2-propanol, 2-
		—	Propylbenzene, N-
		3230	Styrene
		2860	Tetrachloroethylene

*Organic chemical producers data base ID number.

Appendix C

Portable VOC Detection Devices

The three tables listed in this Appendix were taken from:

Environmental Protection Agency (EPA). March 1980. *Summary of Portable VOC Detection Instruments*. EPA 340/1-80-010.

The instruments are classified as ionization detectors, infrared detectors, or combustion detectors. These tables are only a general guide as to the instruments that are being marketed for various uses. Specific applicability for VOC leak detection must be determined by an analyzer's ability to meet the specifications and performance criteria listed in EPA Reference Method 21.

Table C-1. Portable ionization detectors.

Manufacturer	Model no.	Pollutant(s) detected	Principle of operation	Cost ($)	Weight (lb)	Range (ppm)	Accuracy (%)	Sensitivity	Precision (%)	Response time (s)
Analytical Instrument Development, Inc., Avondale, Pennsylvania	550[a] and 551	Nonmethane total hydrocarbons	FID	3711	16.5	0-200 and 0-2000 for Model 550; 0-200 and 0-10,000, for Model 551	± 5	0.1 ppm on a scale of 0-200 ppm	± 5	5
	555[b]	Total hydrocarbons	FID	3987	20.5	0-10,000, 0-2000, and 0-100	± 5	1 ppm on a scale of 0-2000 ppm	± 5	5
	511-12[c]	Total hydrocarbons and individual compounds with GC	FID/GC	4968	41			0.05 ppm as propane		
Bendix, Environmental and Process Instruments Division, Lewisburg, West Virginia	8401[d]	Total hydrocarbons	FID	5195	40	1-1000	± 2	0.01 ppm	± 2	8
Foxboro, S. Norwalk, Conn.	OVA-118	Total hydrocarbons	FID	3500	12	0-10 and 0-100	± 2	0.2 ppm methane	± 2	2
	OVA-128[e]	Total hydrocarbons	FID/GC	4200	12	0-1000	± 2	0.2 ppm methane		
	OVA-98	Total hydrocarbons	FID	3500	12	0-10,000	± 2	0.5 ppm methane	± 2	2
	OVA-108[f]	Total hydrocarbons	FID/GC	4200	12	0-10,000	± 2	0.5 ppm methane		
General Electric, Instrument Products, Lynn, Massachusetts	TVM-1	Halogenated compounds	Ion capture[g]	4060	23	9 ranges: 0-1 through 0-10,000	± 10	0.1 ppm		120
Heath Consultants, Inc., Stoughton, Massachusetts	Detecto PAK II[h]	Total hydrocarbons	FID	2950	8	0-10 0-100 0-1000	j ± 4 j	2 ppm 2 ppm 5 ppm		15

Manufacturer	Model no.	Pollutant(s) detected	Principle of operation	Cost ($)	Weight (lb)	Range (ppm)	Accuracy (%)	Sensitivity	Precision (%)	Response time (s)
HNU Systems, Inc., Newton Upper Falls, Massachusetts	PI-101[a]	Chlorinated hydrocarbons, aromatics, aldehydes, ketones, any substance which adsorption of UV light results in ionization	Photoionization	3395	<9	0-20, 0-200, and 0-2000	−7 −7	1 ppm	5	
Melroy Labs Springfield, Virginia	HC-500	Total hydrocarbons	FID		40	0-10, 0-50, 0-100, 0-500, and 0-1000	±1 on low scale	0.1 ppm CH_4	±1	45
Mine Safety Appliances Co., Pittsburgh, Pennsylvania	Total HC analyzer	Total hydrocarbons	FID	3850	35	0-4 and 0-12,000	±1%			
Survey and Analysis, Inc. Northboro, Massachusetts	Snifty Model A-500[e]	Total hydrocarbons	FID	1695 for basic unit, $2295 for entire portability package	17	0-10 0-100 0-1000 0-10,000	−55 −35 −3 +20	2 ppm		4

[a] A charcoal tube is used to adsorb organics except methane, and a range of 0-10 ppm is available with the recorder. The instrument can be used as alarm by setting in 0-1000 range. This is a screening and leak detection device.
[b] The following features are available: a range of 0-100 ppm with recorder only; internal power, oxygen, and hydrogen supplies; a heated probe; and a battery-operated recorder with a range of 0-100 mV d.c.
[c] Capabilities equal or exceed those of Models 550 and 555.
[d] Capabilities to detect higher concentrations require further investigation. This may be suitable for ambient air measurement only.
[e] Optional GC.
[f] Optional GC.
[g] A heated platinum wire embedded in rubidium combusts incoming gases. Combustion of halogenated materials causes electrons to flow from the rubidium. The electrical flow measured is proportional to the amount of halogenated materials present.
[h] Performance characteristics as measured by NIOSH. Reference 6, Section 3.
[i] Inaccurate.

Table C-2. Portable infrared detectors.

Manufacturer	Model no.	Pollutant(s) detected	Principle of operation	Cost ($)	Weight (lb)	Range (ppm)	Accuracy (%)	Sensitivity	Precision (%)	Response time (s)
Anarad, Inc., Santa Barbara, California	AR-400[a]	Individual species absorbing IR	IR	2395 for an analyzer measuring single gas 5745 for an analyzer measuring three gases (Model 405)			± 1	< ± 1	5	
Astro Resources Corp., Houston, Texas	5000[b]	Individual hydrocarbons	IR		25	Specified by customer, up to 100%	± 1	± 1		
Chrysler Huntsville Electronics Division Huntsville, Alabama	III-C[c]	Total hydrocarbons	IR		20	0-300 and 0-2000 ppm	± 2	± 2	6	
	Mopar[c]	Total hydrocarbons	IR		20	0-300 and 0-2000 ppm	± 2	± 2	6	
	Atlas[c]	Total hydrocarbons	IR		30	0-300 and 0-2000 ppm	± 2	± 2	6	
Foxboro Analytical, Wilks Infrared Center, S. Norwalk, Connecticut	Miran -104[d]	Any species absorbing IR between 2.5 and 14.5 μm in wavelength	IR	Not sold in United States but price may be similar to Miran-1A	24	ppm to percent	± 5	1 ppm		1,4,10, and 40
	Miran-1A	Any species absorbing IR between 2.5 and 14.5 μm in wavelength	IR	6600	32	< ppm to percent	3-4	1-2	1,4,10, and 40	

Manufacturer	Model no.	Pollutant(s) detected	Principle of operation	Cost ($)	Weight (lb)	Range (ppm)	Accuracy (%)	Sensitivity	Precision (%)	Response time (s)
Gas Tech, Inc., Mountain View, California	Halide detector	Halogenated hydrocarbons	Enhancement of radiation from a spark by halogens	1125	13	0-100 and 0-10,000 ppm			5	
Infrared Industries, Inc., Santa Barbara, California	IR-711	Alkane hydrocarbons	IR (solid state detector)	1250	9	0-100% LEL and 0-1000 ppm IR-702, IR-703, and IR-705 are available with analog or digital scales; analog scales range from 0-100% to 0-200 ppm; digital scales range from 0-100% to 0.1%	±5	±5	120	
	IR-702[a]	Any species absorbing IR	IR	2895	34		±1		5	
	IR-703[a]	Any species absorbing IR	IR	2595	34					
	IR-705[a]	Any species absorbing IR	IR	2950	34					
Mine Safety Appliances Co., Pittsburgh, Pennsylvania	LIRA 503[f]	Hydrocarbon species that absorb IR	IR	2970	37	0-100% LEL and 0-1000 ppm		±1	5	

[a] Available in single and dual component versions.
[b] Factory-calibrated for gas to be detected in application.
[c] Autoexhaust analyzers; solid state detectors.
[d] Miran-101 and Miran-103 do not have built-in, multiparameter capabilities. Their measurement range is from 0 to 1000 ppm for most species.
[e] IR-702, IR-703, and IR-705 are usually bench- or panel-mounted instruments. IR-702 is a dual component instrument; and IR-703 and IR-705 are single component instruments.
[f] Can be calibrated to measure a single gas or a mixture if the instrument is panel-mounted.

Table C-3. Portable combustibles detectors.

Manufacturer	Model no.	Pollutant(s) detected	Principle of operation	Cost ($)	Weight (lb)	Range (ppm)	Accuracy (%)	Sensitivity	Precision (%)	Response time (s)
Bacharach Instrument Co., Santa Clara, California	G L H[a] TLV Sniffer[b]	Combustible gases	Catalytic combustion Catalytic combustion Catalytic combustion Catalytic combustion	253 160 279 896	4 4 5 5	0-100% LEL 0-100% LEL 0-100% LEL 0-100, 0-1000, and 0-10,000 ppm	±3	2 ppm	±3	
Biomarine Industries, Inc., Malvern, Pennsylvania	922 900, 900 R, and 900 RS	Combustible gases and vapors Combustible gases and vapors	Catalytic combustion Catalytic combustion	495 685 695, and 715	1.5 3	0-100% LEL 0-100% LEL	±5% LEL. ±5% LEL		5 5	
Control Instruments Corp., Fairfield, New Jersey	FFAP[c]	Flammable gases and vapors	Thermal combustion		28	0-100% LEL	±3	±1	<10	
Gas Tech, Inc., Mountain View, California	1177 1238	Combustible gases Combustible gases	Catalytic combustion Catalytic combustion	525 695	6 7	0-100% LEL 0-100% LEL and 0-500 ppm	±5 ±2	±2 ±2	4 10	
International Sensor Technology, Santa Ana, California	AG5100	Combustible gases and vapors	Change in resistance within detector	1200 for ppm scale, 825 for LEL scale		LEL and ppm	±5	±5	10 on LEL scale and 60 on ppm scale	
Mine Safety Appliances Company, Pittsburgh, Pennsylvania	20[d] 30[e] 40[f]	Combustible gases Combustible gases Combustible gases	Catalytic combustion Catalytic combustion Catalytic combustion	374 374 374	6	0-100% LEL 0-100% LEL 0-10% and 0-100% LEL				

Manufacturer	Model no.	Pollutant(s) detected	Principle of operation	Cost ($)	Weight (lb)	Range (ppm)	Accuracy (%)	Sensitivity	Precision (%)	Response time (s)
Survey and Analysis, Inc. Northboro, Massachusetts	OnMark Model 5[e]	Combustible gases and vapors	Thermal conductivity	285	<5	0-5 and 0-100%	±3		±3	<10
Teledyne Analytical Instruments, San Gabriel, California	980	Total combustibles and oxygen	Catalytic combustion		17	Scale: 0-5% methane; others are available	±2	0.5% of full scale		20

[a] Catalytic combustion (hotwire) in low range and thermal conductivity in high range.
[b] The ranges of TLV can be multiplied by 10 with a dilution probe.
[c] The FFAP uses a propane flame to combust sample gas and is fully portable.
[d] Can be factory calibrated for five gases, such as pentane.
[e] Calibrated to measure natural gas and petroleum vapors in air mixtures.
[f] Factory calibrated for pentane.
[g] Filaments for the 0-100% scale are thermal sensors heated to 300° to 400°F, and filaments for the 0-5% scale are catalytic sensors heated to 1200° to 1300°F.

Appendix D

Number of Fugitive VOC Emission Sources for a Typical Refinery, Chemical Unit and Gas Plant

The three tables in this appendix give an idea of the number of fugitive VOC sources in a typical petroleum refinery, a synthetic organic chemicals plant, and a natural gas/gasoline processing plant. These numbers are estimates based on plant surveys and emission inventory data. In some cases, where emission factors are available, these numbers give an indication of the relative contribution of each equipment type to the total emissions.

Table D-1. Estimated fugitive VOC emissions from a hypothetical 10-unit petroleum refinery (15,900 m³/day capacity).

Equipment type	Number of pieces of equipment	Uncontrolled emissions* (kg/day)	Percentage of total emissions
Pump seals			
Light liquids	125	340	4
Heavy liquids	125	62	1
Valves			
Gas	6,000	3,800	47
Light liquid	9,750	2,500	31
Heavy liquid	9,750	50	1
Safety/relief valves			
Gas	130	500	6
Open-ended lines	1,750	96	1
Flanges	64,000	400	5
Sampling connections	250	90	1
Compressor seals	14	210	3
Totals	93,339	8,048	

* The number of equipment pieces multiplied by their uncontrolled emission factors (given in Table 3-1) yields the uncontrolled emissions per refinery.

Source: Environmental Protection Agency (EPA). April 1982. *VOC Fugitive Emissions in Petroleum Refining Industry—Background Information for Proposed Standard (preliminary draft).*

Table D-2. Fugitive emission sources for three model synthetic organic chemical manufacturing units.

Equipment component[a]	Number of components in unit plant[b]		
	Model A	Model B	Model C
Pump seals			
Light liquid service			
Single mechanical	5	19	60
Double mechanical	3	10	31
Sealless	0	1	1
Heavy liquid service			
Single mechanical	5	24	73
Packed	2	6	20
Valves			
Gas service	90	365	1117
Light liquid service	84	335	1037
Heavy liquid service	84	335	1037
Safety/relief valves			
Gas service	11	42	130
Light liquid service	1	4	13
Heavy liquid service	1	4	14
Open-ended valves and lines[c]			
Gas service	9	37	115
Light liquid service	47	189	581
Heavy liquid service	48	189	581
Compressor seals	1	2	8
Sampling connections[d]	26	104	320
Flanges	600	2400	7400
Cooling towers	[e]	[e]	[e]

[a]Equipment components in VOC service only.
[b]52 percent of existing SOCMI units are similar to Model A.
33 percent of existing SOCMI units are similar to Model B.
15 percent of existing SOCMI units are similar to Model C.
[c]Sample, drain, and purge valves.
[d]Based on 25 percent of open-ended valves.
[e]Data not available.

Source: Environmental Protection Agency (EPA). August 1981. *Control of Volatile Organic Compound Fugitive Emissions from Synthetic Organic Chemical, Polymer and Resin Manufacturing*. Control Technology Guideline (CTG) Draft.

Table D-3. Baseline emissions from three model gas plants.

Component type	Baseline emission factor (kg/day)	Number of components			Baseline emissions (kg/day)			Percent total emissions
		Model plant A (10 vessels)	Model plant B (30 vessels)	Model plant C (100 vessels)	Model plant A	Model plant B	Model plant C	
Valves	0.18 (0.48)	250	750	2500	45 (120)	135 (360)	450 (1200)	57 (59)
Relief valves	0.33 (4.5)	4	12	40	1.3 (18)	4.0 (54)	13 (180)	2 (9)
Open-ended lines	0.34 (0.53)	50	150	500	17 (27)	51 (80)	170 (265)	22 (13)
Compressor seals	1.0 (4.9)	2	6	20	2.0 (9.8)	6.0 (29)	20 (98)	3 (5)
Pump seals	1.2 (1.5)	2	6	20	2.4 (3.0)	7.2 (9.0)	24 (30)	3 (1)
Flanges and connections	0.011 (0.026)	1000	3000	10,000	11 (26)	33 (78)	110 (260)	14 (13)
		Total baseline emissions			79 (204)	256 (610)	787 (2033)	

xx = VOC emission values.
(xx) = Total hydrocarbon emission values.

Source: Environmental Protection Agency (EPA). December 1981. *Control of Volatile Organic Compound Leaks from Natural Gas/Gasoline Processing Plant*. Control Technology Guideline (CTG) Draft.

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16. ABSTRACT

This Student Guidebook is designed for technical personnel involved in monitoring VOC emissions from leaking process equipment. The course reviews in detail the sources of fugitive VOC emissions and the procecdures and equipment used to detect the leaks. Course topics include: overview of regulations, potential sources of VOC emissions, equipment and procedures used to control VOC leaks, portable VOC detection devices, and inspection procedures.

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DISCLAIMER

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SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has promulgated New Source Performance Standards (NSPS) and National Emission Standards for Hazardous Air Pollutants (NESHAP's) for several categories of sources that emit volatile organic compounds (VOC's) and that require monitoring with portable detection instruments. The EPA has also issued control techniques guidelines (CTG's) for a number of source categories that emit VOC's. The source categories covered by the NSPS, NESHAP's, and CTG's include petroleum refineries, synthetic organic chemical plants, coating operations, and natural gas processing plants.

Fugitive VOC emissions at these sources occur at valves, pumps, drains, pressure relief devices, etc. If these points of fugitive emissions can be identified, the leaks can be repaired and the emissions can be eliminated.

This manual presents information on the principles of operation of currently available portable monitors and the field inspection techniques for the monitor's safe use in both screening and compliance determinations. This manual is intended to be used by State or local agencies.

The level of the inspection performed is often determined by the compliance history of the source and the regulatory requirements. If the inspection procedure involves the use of a sophisticated instrument to determine compliance with a regulation, it is classed as a Level 3 inspection, which is the most thorough and time-consuming level. Level 3 inspections are designed to provide a detailed engineering analysis of source compliance by use of measured operating parameters or emissions data. The Level 3 inspection for determining fugitive VOC emissions requires the use of portable hand-held instruments. These instruments include portable organic vapor monitors, thermocouples, and static pressure gauges.

The EPA has published Reference Method 21 to provide a technical method to test for leaks from these sources. Method 21 allows the user to select

one of several instruments available on the market if they meet the specifications and performance requirements, discussed in Section 2. A summary of the published specifications of many of the portable VOC monitors is presented in this manual.

Because the inspector will be using a reference test method and the aquired data may be used in an enforcement action against the facility, special care should be taken in the use of portable instruments during a Level 3 inspection. Calibration procedures must be strictly adhered to verify the acquired data.

SECTION 2

REGULATORY REQUIREMENTS

The use of portable VOC-detecting instruments is based primarily on requirements regarding control of leaks as contained in the NSPS and NESHAP's and in the CTG's published by EPA to provide guidance for State and local agencies in the development of their own regulations.

2.1 NEW SOURCE PERFORMANCE STANDARDS

Two categories of VOC emissions must be monitored: 1) emissions from sources controlled by carbon-bed absorbers, thermal incinerators, and vapor recovery systems; and 2) fugitive emissions from process equipment. Appendix A contains the NSPS requirements for the source categories in Table 1. The monitoring is to be performed as described in 40 CFR 60, Appendix A, Reference Method 21.

2.1.1 Determination of Volatile Organic Compound Leaks From Sources Controlled by Carbon-Bed Absorbers, Condenser Units, and Thermal or Catalytic Incinerators

Carbon-bed absorbers, condenser units, and thermal or catalytic incinerators are used to control emissions from the surface coating of metal furniture, automobiles and light-duty trucks, pressure-sensitive tape and labels, large appliances, metal coils, and beverage cans, and flexible vinyl and urethane coating and printing.

Carbon-bed absorption units, condenser units, and thermal or catalytic incinerators normally require onsite monitoring with stationary instruments rather than portable ones; however, some measurements can be made with portable instruments to verify both the operation of the control equipment and the on-site stationary monitoring results. Carbon-bed absorbers and condenser units require the use of both VOC-detection equipment and temperature-monitoring equipment. Thermal and catalytic incinerators also require the use of temperature monitoring equipment.

TABLE 1. NSPS VOC FUGITIVE (LEAK) EMISSION LIMITS

Source category	Equipment	Emission limit	Monitoring requirement
Subpart VV - Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry	Valves	10,000 ppm by volume (ppmv)	Monthly
	Pumps	10,000 ppmv or visible leak from seal in pumps in liquid service	Monthly
	Compressors	Zero	No requirements
	Sampling connections	Zero	No requirements
	Open-ended lines	Zero	No requirements
	Pressure-relief devices Exception: plants processing only heavy liquids or solids and facilities producing beverage alcohol	500 ppmv or less above background level	Periodic[a]
Subpart XX - Bulk Gasoline Terminals	All the loading racks at a bulk gasoline terminal that deliver gasoline into any delivery tank truck	10,000 ppmv	Monthly
Subpart GGG - Equipment Leaks of VOC in Petroleum Refineries	Valves	10,000 ppmv	Monthly
	Pumps	10,000 ppmv or visible leak	Monthly
	Sampling connections	Zero	No requirements

(continued)

TABLE 1 (continued)

Source category	Equipment	Emission limit	Monitoring requirement
	Open-ended lines	Zero	No requirements
	Pressure relief device	500 ppmv or less above background level	Periodic[a]
Subpart KKK - Equipment Leaks of VOC from Onshore Natural Gas Processing Plants	Valves	10,000 ppmv	Monthly
	Pumps	10,000 ppmv	Monthly
	Sampling connections	Zero	No requirements
	Open-ended lines	Zero	No requirements
	Pressure relief devices	10,000 ppmv	Periodic[a]

[a]Except in the case of pressure releases where the source must be monitored within 5 days of a pressure release.

In certain source categories, the NSPS regulations require adherence to an emission limit or some other operating parameter. Compliance with this requirement is monitored by onsite equipment. These standards apply to various surface coating operations and flexible vinyl and urethane coating and printing (Table 2).

Portable monitoring instruments can be used on the exit vent/stack side of the carbon absorbers and condenser units to detect breakthrough of the VOC's. A portable monitor used to perform this type of test must be sensitive in the 50 to 500 ppmv range. Such an instrument can detect VOC emissions that are over and above what would be expected from a controlled source. Because these portable instruments are continuous or semicontinuous, the probe only has to be put in the gas stream for the length of time necessary to exceed the response time specified in the instrument manual.

TABLE 2. NSPS VOC MONITORING REQUIREMENTS FOR SOURCES CONTROLLED BY CARBON-BED ABSORBERS AND THERMAL OR CATALYTIC INCINERATION

Source category	Equipment or operations	Emission limit or work practice	Monitoring requirements
Subpart EE - Surface Coating of Metal Furniture	All metal furniture surface coating operations applying organic coatings	0.90 kg/liter of coating solids applied	Temperature measurement with capture system and incineration
Subpart MM - Automobile and Light-Duty Truck Surface Coating Operations	Prime coating	0.16 kg/liter of applied coating solids per each prime coat operation	Permanent record of incinerator temperature, if applicable
	Guide coating	1.40 kg/liter of applied coating solids per each guide coat operation	Same as above
	Top coating	1.47 kg/liter of applied coating solids per each top coat operation	Same as above
	Exempt: plastic components and all-plastic bodies on separate lines		Same as above
Subpart RR - Pressure-Sensitive Tape and Label Surface Coating	Coating line inputing greater than 45 Mg (50 tons) VOC per 12-month period	0.2 kg of VOC per kg of coating solids applied or	Facilities with thermal incinerators: temperature of incinerator's exhaust gases
		90% VOC emission reduction or an overall emission reduction equivalent to the 0.20 kg per kg of coating solids applied, whichever is less stringent	Facilities with catalytic incinerators: gas temperature upstream and downstream of the catalyst bed

(continued)

TABLE 2 (continued)

Source category	Equipment or operations	Emission limit or work practice	Monitoring requirements
	Coating line inputting less than 45 Mg (50 tons) VOC per 12-month period	Not subject to limits but subject to monitoring requirements	
Subpart SS - Industrial Surface Coating: Large Appliances	All large appliance surface coating line operations	0.90 kg/liter applied coating solids	Temperature measurement with capture system and incineration
Subpart TT - Metal Coil Surface Coating	Prime coating operations, finish coating operations, and combined prime and finish coating operations when finish coat is applied wet on wet over prime coat and cured simultaneously	0.28 kg/liter coating solids with no emission control	Continuous record of incinerator temperature, if applicable
		0.14 kg/liter coating solids with continuous emission control	Same as above
		10% VOC's applied (90% emission reduction)	Same as above
		Prorated value with intermittent emission control	Same as above
Subpart WW - Beverage Can Surface Coating Industry	Two-piece beverage can coating:		
	Exterior base coating operation	0.29 kg VOC/liter of coating solids (except clear base coating)	Temperature measurement for incineration
	Clear base coating or overvarnish coating	0.46 kg VOC/liter of coating solids	Same as above

(continued)

TABLE 2 (continued)

Source category	Equipment or operations	Emission limit or work practice	Monitoring requirements
	Inside spray coating	0.89 kg VOC/liter of coating solids	Temperature measurement for incineration
Subpart FFF - Flexible Vinyl and Urethane Coating and Printing	Rotogravure printing line	Reduce gaseous VOC emissions by 85%	Continuous measurement and recording of the temperature of thermal incinerator exhaust gases or of the gas temperature upstream and downstream of a catalytic incinerator, installation of a continuous monitoring system for solvent recovery

Portable monitors also can be used to check the continuous monitor required at some sources. This measurement process is the same as that used for testing breakthrough.

A thermocouple can be used to check the exit gas temperature from a thermal or catalytic incinerator. A baseline stack temperature measurement should be taken at the time the incinerator's permanent thermocouple is calibrated. This baseline temperature measurement gives a reference point for future inspections.

2.1.2 Fugitive Emissions From Process Equipment

For the synthetic organic chemicals manufacturing industry, bulk gasoline terminals, petroleum refineries and on-shore natural gas processing plants (Table 1), NSPS requires periodic leak inspections of the equipment to determine if any fugitive VOC emissions are escaping. These leak inspections are performed with portable VOC-detecting equipment according to Reference Method 21. Equipment to be tested includes valves, pumps, seals, compressors, sampling connections, open-ended lines, and pressure-relief devices.

A portable VOC-detection monitor may be used for leak inspections. The probe must be inserted in the vicinity of a potential leak and must be moved around the area where the leak may occur. The leak must be compared against a background concentration, especially when the standards call for an emission limit of 0 or 500 ppmv. Field procedures for conducting leak inspection monitoring are discussed in Section 6 of this manual.

2.2 NATIONAL EMISSION STANDARDS FOR HAZARDOUS POLLUTANTS

For certain categories of sources, NESHAP's place a not-to-be-exceeded limit on fugitive emissions from processes, pumps, compressors, valves, pressure-relief systems, etc. These standards apply to vinyl chloride, ethylene dichloride, benezene, and volatile hazardous air pollutants (VHAP).

Emissions are monitored both by stationary onsite monitors and portable instruments, depending on the regulatory requirements. Table 3 lists the regulated facilities, emission standards (where monitoring is required), and monitoring requirements for fugitive emissions from process sources. The methods of detecting leaks and types of equipment to be inspected for leaks

TABLE 3. NESHAP MONITORING REQUIREMENTS FOR FUGITIVE EMISSIONS

Source category	Equipment or operations	Emission limit or equipment standard	Monitoring requirements
Subpart F - Vinyl Chloride	Ethylene dichloride manufacture	1) Ethylene dichloride purification: 10 ppmv[a] 2) Oxychlorination reactor: 0.2 g/kg (0.0002 lb/lb) of the 100% ethylene dichloride product	Source test Continuous monitor Source test Continuous monitor
	Vinyl chloride manufacture	10 ppmv[a]	Source test Continuous monitor
	Polyvinyl chloride manufacture		
	Reactor; stripper; mixing, weighing and holding containers; monomer recovery system	10 ppmv[a]	Source test Continuous monitor
	Reactor opening loss	0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride/lb)	Source test Continuous monitor
	Reactor manual vent	No emissions	
	Sources following stripper	For each calendar day: 1) Using stripping technology - 2000 ppmv for polyvinyl chloride dispersion resins (excluding latex), 400 ppmv	Source test

(continued)

TABLE 3 (continued)

Source category	Equipment or operations	Emission limit or equipment standard	Monitoring requirements
		each for other polyvinyl chloride resins (including latex)	
		2) Other than stripping technology - 2 g/kg (0.002 lb/lb) product for dispersion polyvinyl chloride resins (excluding latex) 0.4 g/kg (0.0004 lb/lb product for other polyvinyl chloride resins (including latex)	Source test
	Ethylene dichloride, vinyl chloride and/or polyvinyl chloride manufacture		
	Relief valve discharge	No discharge	No requirement
	Loading and unloading lines	0.0038 m^3 after each loading, or 10 ppm when contained by a control system	Source test Continuous monitor
	Slip gauges	10 ppm from the required control system	Source test Continuous monitor
	Pump; compressor and agitator seal	10 ppm from the required control system with seals	Source test Continuous monitor

(continued)

TABLE 3 (continued)

Source category	Equipment or operations	Emission limit or equipment standard	Monitoring requirements
	Leakage from relief valves	Rupture disk must be installed	No requirement
	Manual venting of gases	10 ppmv from a required control system	Source test Continuous monitor
	Opening of equipment	10 ppmv from a required control system	Source test Continuous monitor
	Samples (at least 10% by weight vinyl chloride)	Returned to system	No requirement
	Leak detection and elimination	Implementation of an approved program	Approved testing program
	In-process wastewater	10 ppmv before discharge	Source test Continuous monitor
Subpart J - Equipment Leaks (Fugitive Emission Sources) of Benzene	Pumps	No leakage (instrument reading <10,000 ppmv)	Monthly leak detection and repair program
	Compressors	Meet equipment specifications	No requirement
	Pressure-relief devices	No detectable emissions	No requirement
	Sampling connec-systems	No VHAP emissions Meet equipment specifications	No requirement
	Open-ended valves or lines	Meet equipment specifications	No requirement

(continued)

TABLE 3 (continued)

Source category	Equipment or operations	Emission limit or equipment standard	Monitoring requirements
	Valves	No leakage (instrument reading <10,000 ppmv)	Monthly leak detection and repair program
	Pressure-relief devices in liquid service and flanges and other connectors	No leakage (instrument reading <10,000 ppmv)	No requirement
	Product accumulator vessels or systems designed to produce or use >1,000 Mg/yr benzene	Meet equipment specifications	No requirement
	Closed-vent systems	No detectable emissions	No requirement
	Control systems:		
	Vapor recovery systems	Operate at 95% efficiency	No requirement
	Enclosed combustion devices	Operate at 95% efficiency	No requirement
	Flares	No visible emissions	No requirement
Subpart V - Equipment Leaks (Fugitive Emission Sources)	Pumps, compressors, pressure relief devices, sampling connection systems, open-ended valves or lines, valves, flanges and other	Same as Subpart J	Same as Subpart J

(continued)

TABLE 3 (continued)

Source category	Equipment or operations	Emission limit or equipment standard	Monitoring requirements
	connectors, product accumulator vessels, and control devices		

[a]Before opening any equipment for any reason, the quantity of vinyl chloride is to be reduced so that the equipment contains no more than 2.0% by volume vinyl chloride or 0.0950 m^3 (25 gal) of vinyl chloride, whichever is larger, at standard temperature and pressure.

are similar to those presented in Subsection 2.1.2. Table 3 also presents the requirements for leak detection and the emission limits. It should be noted that because vented discharges from NESHAP sources are controlled with thermal or catalytic incineration devices, these sources are monitored with temperature sensing devices. Appendix A contains the NESHAP's that are listed in Table 2.

2.3 INSTRUMENT SPECIFICATIONS

Limited portable VOC-detection instruments specifications are outlined in Appendix A of 40 CFR 60. The reader is encouraged to review Reference Method 21 (Appendix A) to become familiar with the required instrument specifications. It should be noted that no specifications concerning other types of instruments such as thermocouples and static pressure gauges are currently available.

SECTION 3

PORTABLE INSTRUMENT OPERATING PRINCIPLES

Various types of instruments are available for detecting organic vapors during inspections. These monitors involve a variety of detectors that operate on several different principles. Each detector has its own advantages, disadvantages, and sensitivity.

Other types of portable equipment used during source inspections include temperature monitors, flow monitors, and pressure gauges. This equipment is much smaller, less expensive, and easier to use than the portable VOC detectors.

3.1 VOC DETECTORS

Several types of portable VOC detectors can be used either as screening tools or to meet the requirements of EPA Method 21. These include:

- o Flame ionization detector (FID)
- o Photoionization (ultraviolet) detector (PID)
- o Nondispersive infrared detector (NDIR)
- o Catalytic combustion or hot wire detector.

The specifications of these instruments vary greatly with regard to sensitivity, range, and responsiveness. Table 4 lists the most common monitors currently in use and the associated detection principle, range, sensitivity, and response time of each.

3.1.1 Flame Ionization Detector

In an FID, the sample is introduced into a hydrogen flame. A concentration of even 0.1 ppm of a hydrocarbon produces measurable ionization, which is a function of the number of carbon ions present. A positively charged collector surrounds the flame, and the ion current between the flame and the collector is measured electronically. Pure hydrogen burning in air produces

TABLE 4. MOST COMMON PORTABLE VOC DETECTION INSTRUMENTS[a]

Monitor	Detection principle	Range, ppm	Sensitivity	Response time, s
550, 551, 555 (AID, Inc.)	FID	0-200, 0-2000, 0-10,000	0.1 ppm at 0-200 ppm	5
OVA 108, 128 Century Systems, Inc. (Foxboro)	FID	0-10, 0-100, 0-1000	0.2 ppm (Model 128) 0.5 ppm (Model 108)	2 2
PI-101 (HNu Systems, Inc.)	PID	0-20, 0-200, 0-2000	1 ppm	5
TLV Sniffer (Bacharach)	Catalytic combustion	0-500, 0-5000, 0-50,000	2.0 ppm	
Ecolyzer 400 (Energetics Science)	Catalytic combustion	0-100% LFL	1% LFL[b]	15
Miran 1A (Foxboro)	IR	ppm to %	1 ppm	1, 4, 10 and 40

[a]Does not necessarily represent all portable monitors currently being sold.
[b]Lower flammability limit.

very little ionization, so background effects are essentially masked by the hydrogen flame. The calibrated output current is read on a panel meter or chart recorder.

Organic compounds containing nitrogen, oxygen, or halogen atoms give a reduced response when compared to compounds without these atoms. The FID hydrocarbon analyzers are usually calibrated in terms of a gas such as methane or hexane, and the output is read in parts per million of carbon measured as methane or hexane.

Although nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), and water vapor (H_2O) do not produce significant interferences, condensed water vapor can block the sample entry tube and cause erratic readings. Also, when oxygen (O_2) exceeds 4 percent, a significantly lower output reading can occur.

The relative response of the FID to various organic compounds, including those with attached oxygen, chlorine, and nitrogen atoms, varies from compound to compound.

3.1.2 Photoionization Detectors

In the photoionization process, ultraviolet light ionizes a molecule as follows: $R + h\nu \rightarrow R^+ + e^-$, where R^+ is the ionized species and hv represents a photon with energy less than or equal to the ionization potential of the molecule. Generally all species with an ionization potential less than the ionization energy of the lamp are detected. Because the ionization potential of all major components of air (O_2, N_2, CO, CO_2, and H_2O) is greater than the ionization energy of the lamps in general use, they are not detected.

The sensor consists of an argon-filled, ultraviolet (UV) light source that emits photons. A chamber adjacent to the sensor contains a pair of electrodes. When a positive potential is applied to one electrode, the field that is created drives any ions formed by the absorption of UV light to the collector electrode, where the current (proportional to the concentration) is measured.

3.1.3 Nondispersive Infrared Detector

Nondispersive infrared (NDIR) spectrometry is a technique based on the broadband absorption characteristics of certain gases. Infrared radiation is typically directed through two separate absorption cells: a reference cell and a sample cell. The sealed reference cell is filled with nonabsorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of the gas being analyzed. When a particular hydrocarbon is present, the IR absorption is proportional to the molecular concentration of that gas. The detector consists of a double chamber separated by an impermeable diaphragm. Radiant energy passing through the two absorption cells heats the two portions of the detector chamber differentially. The pressure difference causes the diaphragm between the cells in a capacitor to distend and vary. This variation in capacitance, which is proportional to the concentration of the component of gas present, is measured electronically.

The NDIR instruments are usually subject to interference because other gases (e.g., H_2O and CO_2) absorb at the wavelength of the gas of interest. Efforts to eliminate the interferences by use of reference cells or optical filters are only partially successful. For hydrocarbon (HC) monitoring, the detector is filled with one or several different hydrocarbons, which may be different from the HC contained in the sample; this causes a disproportionate response. Other sources of errors include gas leaks in the detector and reference cells, inaccurate zero and span gases, nonlinear response, and electronic drift.

3.1.4 Catalytic Combustion or Hot Wire Detector

The heat of combustion of a gas is sometimes used for quantitative detection of that gas. Suffering the same limitation as thermal conductivity, this method is nonspecific, and satisfactory results depend on sampling and measurement conditions.

One type of thermal combustion cell uses a resistance bridge containing arms that are heated filaments. The combustible gas is ignited in a gas cell upon contact with a heated filament; the resulting heat release changes the filament resistance, which is measured and related to the gas concentration.

Another combustion method uses catalytic heated filaments or oxidation catalysts. Filament temperature change or resistance is measured and related to gas concentrations.

3.2 THERMOCOUPLES

The temperature monitors most commonly used are direct-readout hand-held thermocouples. The thermocouple is composed of two wires of dissimilar metals that are joined at one end. When the joined end is heated, a voltage flow can be observed (Seebeck effect). A voltmeter is attached to the thermocouple, and the observed voltage is proportional to the measured temperature. A portable thermocouple assembly consists of a shielded probe, a connecting wire, and a voltmeter. The voltmeter may be a temperature conversion unit on a multimeter or a dedicated direct readout temperature unit. The voltmeter is battery-operated, small, and easily portable.

3.3 STATIC PRESSURE GAUGES

Among the several different available static pressure gauges, the most commonly used for this type of field work are the inclined manometer and the diaphragm gauge. A pressure tap is necessary for use of a portable static pressure gauge. The pressure tap basically consists of a small opening in the wall of a duct, which can be fitted with a connection and a hose to make pressure measurements. The tap should be far enough away from such disturbances as elbows and internal obstructions to make the effects of such disturbances negligible.[4]

The appropriate side, positive or negative, of the manometer or pressure gauge is connected by a rubber hose at the tap, and a pressure reading can be taken. It is often advantageous to disconnect a permanent pressure gauge and take a pressure reading at that point to compare it with the facility's instrumentation.

SECTION 4

ESTABLISHING AN AGENCY PROGRAM FOR THE USE OF PORTABLE INSTRUMENTS FOR MONITORING VOC AND AIR TOXICS SOURCES

The portable instruments used during VOC and air toxics source inspections require special care and attention to ensure that they provide results that are consistent with the agencies overall goal and objectives. A well developed and organized program is necessary to ensure selection of the proper instruments and adequate calibration procedures; the adoption of written measurement and recordkeeping procedures; and the taking of sufficient field notes during inspections. The purpose of this section is to help a regulatory agency establish a complete program for the use of portable instruments for VOC source inspections.

Factors to consider during the preparation of bid specifications include the instrument performance requirements of the promulgated regulations and the practical features that improve the instrument's reliability and make it more convenient to use. Detailed information is necessary concerning the type of laboratory and shop facilities that will be needed to support portable inspection instruments. These instruments should not be calibrated, maintained, and stored in an office.

4.1 SELECTION OF THE NECESSARY TYPES OF INSTRUMENTS

Selection of the types of instruments needed for source evaluation is based primarily on a review of the types of industrial facilities within the agency's jurisdiction and an evaluation of the inspection requirements inherent in the promulgated VOC regulations. Agencies should also determine if it is possible to select instruments that can be used for future air toxic control requirements as well as the already existing VOC regulations.

4.1.1 Organic Vapor Analyzers

Detector's Response--

One important criterion in the selection of organic vapor detectors is the response of the instrument to the specific chemical or chemicals present

in the gas stream. The abilities of the major classes of organic vapor analyzers to detect different organic chemicals differ substantially. The response factor, defined below, provides a convenient index of this property.

Response Factor = Actual Concentration/Instrument Observed Concentration

A response factor of 1.0 means that the instrument readout is identical to the actual concentration of the chemical in the gas sample. As the response factor increases, the instrument readout is proportionally less than the actual concentration. If the regulatory limit is 10,000 ppmv (observed), the use of an instrument with a response factor of 10 for the specific chemical(s) would allow an actual concentration of 100,000 ppmv. Conversely, the use of an instrument with a response factor of 0.1 would indicate that the regulatory limit of 10,000 ppmv had been exceeded when the actual concentration is only 1000 ppmv. It is desirable to select an instrument with response factors as close as possible to 1.0 for the specific compounds of interest.

Unfortunately, instrument response factors can be complex functions of numerous variables. The response factors depend on the chemical compound used to calibrate the organic vapor detector and on the concentration of organic vapor being analyzed.[5,6] Published response factors that specify the value based on the instrument-determined concentration are preferred in the selection of an instrument because they are the most consistent with the regulatory format.

Fugitive leaks often will involve mixtures of organic vapors. Work done by Brown, Dubose, and Harris indicated that the response factor for a mixture of two organic compounds falls between the individual response factors for the compounds.[7] This would suggest that the instrument offers no synergistic phenomenon and that weighted average response factors could be used to approximate instrument response to a mixture.

Representatives of instrument manufacturing companies contacted as part of this study generally believe that the response factors published by EPA and by their companies are sufficiently accurate.[19,21,39] Slight differences, however, do exist between response factors determined by EPA and those reported by instrument manufacturers. These differences could be due to differences in the calibration procedures, the specific instrument model used in the work, or the specific instrument itself. Many instrument manufacturers, however,

believe that instrument-to-instrument variability in the response factors is slight and that the values remain relatively stable over the life of the instrument.[19,21,39,40] Neither the EPA nor the instrument manufacturing companies, however, have specifically studied instrument-to-instrument variability or long-term response factor stability. One consulting firm has recommended that users routinely redetermine the response factors rather than relying on published values.[24] There are some who believe that routine redetermination of instrument-specific response factors by regulatory agencies is unnecessary in most cases. The most recent response factor data published by both EPA and the instrument manufacturers should be consulted before instruments are purchased. The response factor data compiled in Appendix B should assist regulatory agencies in their evaluation of the general capabilities of different styles of instruments. These data include a partial listing of the response factors determined for the Foxboro OVA-108 and the Bacharach TLV Sniffers.[5,6] Limited response factor information concerning photoionization analyzers and one infrared analyzer has been abstracted from other sources.[8,9]

A review of the response factor data shown in Appendix B indicates that a substantial difference exists among the four major categories of VOC instruments. The instruments capable of monitoring high concentrations of hydrocarbon compounds, which make up many of the VOC emissions, are not as useful for measuring some of the oxygenated and chlorinated organic compounds, which represent many of the air toxic emissions. Thus, it may be impossible to reconcile the needs of both the VOC and air toxics inspection programs by the selection of a single type of instrument.

Because response factor data are currently very limited, agencies may wish to use additional data in selecting organic vapor analyzers. In the case of photoionization units, the ionization potentials of organic compounds provide a qualitative index of the instrument's capability to detect the compound. A summary of ionization potential data provided by an instrument manufacturer[10] is provided in Appendix C. In reviewing these data, the agency should note that an instrument often can detect compounds with ionization potentials slightly above the rating of the lamp. For example, a compound with an ionization potential of 10.5 eV could possibly be monitored with an

instrument having a 10.0 eV lamp.[11] Although the lamp's rating is based on the wavelength of the most intense emission line, there are often less intense emission lines at shorter wavelengths.

Range and Accuracy--

The ability of an instrument to measure 10,000 ppmv should be carefully considered if the instrument will be used to determine compliance with EPA Method 21 regulations. As indicated in Table 4, only a few of the currently available units can operate at 10,000 ppmv or above. Other units can operate at this concentration only by using dilution probes. Although dilution probes can be used accurately, they can also be a large source of error. Both changes in flow rate through the dilution probe and saturation of the charcoal tubes used to remove organic vapors from the dilution air can lead to large errors in the indicated organic vapor concentration. Dilution probes also complicate calibration and field span checks. For these reasons, they should be avoided whenever possible.

Generally, the instruments should have the desired accuracy at the concentration of interest. It should be noted that an accuracy of ± 5 percent is required for Method 21 work.

Ease-of-Use--

Ease of use is an important instrument selection criterion because of the conditions under which the field inspector must work. The instrument must be as light as possible because the inspector must walk over relatively large areas (in most facilities) to evaluate fugitive leaks from numerous valves and other sources. In some cases, a moderate amount of climbing is also necessary. After 4 to 6 hours, even a light instrument can seem uncomfortably cumbersome.

Table 5 contains information concerning the portability of some of the commercially available organic vapor instruments. As shown, the weights of the units and the manner in which they are used differ substantially.

Generally, instruments equipped with shoulder straps are the most convenient to use for fugitive VOC leak surveys.[11] The instrument readout on the hand-held probe is very important, because the inspector immediately sees when the probe has been placed in a very high VOC concentration. The hand-held gauge also slightly reduces the time involved in leak surveys.

TABLE 5. EASE-OF-USE OF ORGANIC VAPOR ANALYZERS

Instrument manufacturer	Type	Weight, lbs	Mode of use	Other comments
Century (Foxboro) 108	FID	13	Shoulder strap	Readout on probe
Century (Foxboro) 128	FID	13	Shoulder strap	Readout on probe Necessary to remove cover to adjust range
Photovac 10S50	PID	26	Case with handle	Necessary to open case at each measurement site
HNU PI-101	PID	9	Shoulder strap	
AID Model 585	PID	8	Small case with handle	
AID Model 712	FID	14	Shoulder strap	Readout on probe
Barachach TLV	Catalytic	5.5	Shoulder strap	
Ecolyzer 400	Catalytic	8	Shoulder strap	
Miran 1A	Infrared	12.5	Carrying handle	Necessary to set unit down at each measurement site

Intrinsic Safety--

All instruments used during field inspections of VOC source and air toxic sources must be intrinsically safe if they are to be used in potentially explosive atmospheres. Localized pockets of gas (and even particulates) within the explosive range can result from fugitive leaks and malfunctioning control devices. Intrinsic safety simply means that the instrument will not provide a source of ignition for the explosive materials when the instrument is used properly. Instrument designs are certified as intrinsically safe for certain types of atmospheres by organizations such as the Factory Mutual Research Corporation. Table 6 lists the types of atmospheres by safety classification. The conditions can be further classified according to Groups A through G,

TABLE 6. DEFINITIONS OF HAZARDOUS LOCATIONS IN ACCORDANCE WITH THE NATIONAL ELECTRICAL CODE[a]

Classification	Description
Class I locations	Areas where volatile flammable liquids and flammable gases are used and handled.
Division 1	Class I areas where hazardous concentrations are likely to occur in the course of normal operations.
Division 2	Class I areas where hazardous concentrations are probable only in the case of accidents or unusual operating conditions.
Class II locations	Areas where combustible dust may be present.
Division 1	Class II areas where combustible dust is likely to be present in explosive or ignitable concentrations in the course of normal operations.
Division 2	Class II areas where hazardous concentrations of combustible dust is probable only in the case of accidents or unusual operating conditions.
Class III locations	Areas where easily ignited fibers and materials that could result in combustible flyings are present.
Division 1	Class III areas where easily ignited fibers and materials are processed.
Division 2	Class III areas where easily ignited fibers and materials are stored or handled.

[a]Sources: References 12 and 13.

which denote the type of flammable vapor or combustible dust that may be present.

The large majority of the organic vapor analyzers are designed to be instrinsically safe in Class 1 areas. Factory Mutual, however, has certified only a few of the currently available commercial instruments to be intrinsically safe. Table 7 lists the present status of commercial instruments.

It should be noted that the information presented in Table 7 could change in the near future. At least one manufacturer has several applications pending concerning hazardous location approval.[14]

TABLE 7. INTRINSIC SAFETY RATINGS OF COMMERCIAL INSTRUMENTS, JANUARY 1986[a]

Instrument manufacturer	Model	Atmosphere	Factory mutual approved
Foxboro	OVA-108	Class I, Division 1	Yes
Foxboro	OVA-128	Class I, Division 1	Yes
Bacharach	TLV[b]	Class I, Division 1 and 2	Yes
AID, Inc.	585	Class I, Division 2	No
AID, Inc.	712	Class I, Division 1	No
HNU Systems, Inc.	PI-101	Class I, Division 2	No

[a]Not a complete listing of commercial instruments.
[b]Model 0023-7356.

Other Considerations--

Several recent improvements have been made in probe design. As a result, agencies should carefully evaluate the probes available with the organic vapor analyzer models they are considering. By reviewing detailed drawings or examining "loaner" probes, agencies can determine if the probe is susceptible to leakage. Air infiltration through the probe has been a common problem in the past.[15,16,17,18] This problem has been especially severe on telescoping-type extension probes.

Some older flame ionization analyzers have suffered hydrogen leaks due to cold creep of the TEFLON washers used to seal part of the pressurized hydrogen line.[18,19] The hydrogen leak ignition problems reported in earlier studies,[11] however, may have been solved by redesigning the hydrogen line fittings.[19] Agencies should examine the hydrogen line design on any FID that is being seriously considered for purchase to ensure that this will not be a problem.

4.1.2 Thermocouples

It should be noted that currently none of the battery-powered thermocouples are designed as intrinsically safe for either Class I or Class II atmospheres. Therefore, these instruments cannot be taken into or through

areas where there is a possibility of encountering explosive mixtures of organic vapor and/or dust. Conventional flashlights are also not intrinsically safe, and they should be replaced by explosion-proof flashlights.

4.2 INSTRUMENT SPARE PARTS AND ACCESSORIES

Portable instruments for inspection of VOC sources and air toxic sources are sophisticated units. Maintaining an available supply of certain accessory spare parts and routine replacement parts will minimize unnecessary downtime of these instruments and will help field inspectors to obtain high quality data.

4.2.1 Battery Packs

All of the organic vapor analyzers require a rechargable battery pack to operate the sample pump and the electrical components. Failure of these battery packs is a common problems with these instruments.[11,15,16] A replacement battery pack should be taken along on all field inspections in case an unexpected failure should occur. A spare is also useful when field work is being conducted during cold conditions, as such conditions reduce the useful operating time.[19]

A spare recharger is also necessary for the lead-acid gel battery packs used in some types of flame ionization analyzers, as these batteries must be recharged on an almost continuous basis to prevent loss of the charge. If a deep discharge occurs, the battery pack cannot be recharged by the unit supplied with the instrument.[19] Thus, two rechargers are needed, one for the original instrument battery pack and one for the backup battery pack.

Spare rechargers are also recommended for the nickel-cadmium (Ni-Cd) battery packs commonly used in the photoionization instruments. Recent improvements in battery rechargers have significantly reduced the possibility of battery overcharge.[20] Only these newer style units should be used if the instrument has the Ni-Cd batteries.

A nonrechargable 9-volt battery similar to those used in radios, is normally used in a thermocouple. As a result, a spare is recommended.

4.2.2 Detectors

The photoionization analyzers and the catalytic combustion analyzers have detectors that must be replaced after extended use. The inspectors should take replacement detectors with them on field trips in case they are needed.[17,21]

For photoionization units, the key component is the ionization lamp within the detector. Inspectors should take at least one spare lamp on all field work in the event that one of the following may occur: the lamp is damaged by the deposition of nonvolatile components on the lamp window, the window is scratched during cleaning, the lamp is damaged by physical shock, or the lamp simply wears out.

The detectors of catalytic combustion analyzers are composed of a coated hot wire that is part of a Wheatstone bridge. Exposure to high concentrations of organic vapor can cause excessive volatilization of the catalyst from the wire surface.[21] The sensor also can be damaged by the deposition of nonvolatile, noncombustible material. For these reasons, at least two replacement sensors should be taken on field inspections.

4.2.3 Particulate Filters

All organic vapor analyzers are subject to damage by the deposition of nonvolatile materials in the instrument probes and/or the instrument detectors. Most commercially available units include some form of particulate filters within the probes to collect this material. Several replacement filters should be taken along with the instruments because the filters are easily blinded.

Most experienced instrument operators consider it prudent to use a glass wool "Prefilter" in addition to the instrument filters to reduce further the chances of particulate deposition inside the instruments.[11,16,17] A small section of plastic tubing with some glass wool is recommended for all organic vapor analyzers. Care must be taken, however, to ensure that the filter does not add excessive sample flow resistance.

4.3 LABORATORY AND SHOP SUPPORT FACILITIES

Because of their level of sophistication, organic vapor analyzers require laboratory and instrument shop support facilities. Regulatory agency inspectors should not attempt to store and calibrate the instruments in their

offices, as this practice can lead to significant safety problems and complicate the routine maintenance of the instruments.

4.3.1 Storage of Compressed Gases

One of the primary purposes of the laboratory facility is to provide a safe location for storage of the gas cylinders used to calibrate the organic vapor analyzers. These facilities are able to secure the cylinders firmly so they cannot be knocked over accidently. Accidents involving even small gas cylinders in offices could have very serious consequences. Furthermore laboratories can and should store the cylinders in areas that are properly ventilated with exhaust hoods. Conversely, leaks of compressed gas in offices can lead to localized high concentrations of gases such as hexane, benzene, butadiene, and vinyl chloride, or even to localized pockets of explosive gas mixtures. For these reasons, it is very important to store and use the calibration cylinders, zero gas cylinders, and hydrogen cylinders (for flame ionization analyzers) in properly designed laboratory facilities.

Another important consideration is that the exhaust from organic vapor analyzers during calibration can be toxic. In the case of the photoionization analyzers, most of the inlet calibration gas is exhausted because the instruments are nondestructive. In the case of flame ionization detectors, however, low concentrations of phosgene and hydrogen chloride can be emitted when chlorinated hydrocarbons are used for calibration.[22] Thus, the instrument should be placed in a location where the exhaust is captured by an approved hood and ventilation system.

4.3.2 Gas Flow Evaluation

Many of the organic vapor analyzers, especially the flame ionization detectors, are sensitive to the sample gas flow rate. Routine confirmation of proper flow rate is important, especially for those instruments that do not include a flow sensor. Flow rates are normally measured by use of a rotameter designed for flow rates between 0.5 and 5.0 liters per minute. The rotameter should be calibrated against a soap bubble flow meter.

4.3.3 Electrical Diagnostic Equipment

The extent to which malfunctioning organic vapor analyzers can be serviced by agency personnel is limited because the intrinsic safety of the

instrument can be voided inadvertently. Nevertheless, qualified agency instrument technicians should be equipped to check such basic operating parameters as the lamp voltages of photoionization units and the battery output voltages on all portable instruments.

4.3.4 Thermocouple Calibration Equipment

The thermocopule readout device and thermocouple probes should be calibrated at least twice a year. For convenience, the calibrations should be performed in-house with a conventional tube furnace. The field instrument and probes are compared against National Bureau of Standards (NBS) traceable thermocouple probes.

4.3.5 Static Pressure Calibration Equipment

All diaphragm-type static pressure gauges must be calibrated on at least a weekly basis. A relatively large U-tube manometer should be permanently mounted in the agency laboratory for calibration of 0 to 10 inch W.C. and the 0 to 60 inch W.C. gauges.[23] An inclined manometer is needed for calibration of the 0 to 2 inch W.C. gauges.

4.3.6 Storage Space

Adequate space should be provided to store the instruments, the necessary spare parts, and the routine calibration/maintenance records. The availability of convenient storage space removes the temptation to store the instruments in the trunk of a car, where they could be damaged by excessive vibration and shock or by excessive heat. A checklist should be posted near the stored units listing the spare parts that should be taken to jobsites to ensure adequate instrument performance during the inspection.

Adequate working area should be provided for the inspectors to calibrate and check-out the instruments before leaving for the field. The working area must be large enough to accommodate a 20 to 30 liter TEDLAR bag, the instrument, the gas cylinders, and any gas-blending equipment that may be necessary.

4.4 INSTRUMENT MAINTENANCE PROGRAM AND RECORDS

In most regulatory agencies, numerous individuals will use the portable organic vapor analyzers, thermometers, and static pressure gauges, and it is

unrealistic to expect all of them to be fully knowledgeable concerning instrument calibration and repair. It is also unrealistic to ask each of them to make independent determinations of organic vapor analyzer response factors or other performance data obtained on an infrequent basis. Therefore, one or two people should be assigned the responsibility for the overall maintenance of the instruments. Persons skilled in instrument calibration and/or repair are ideal for this assignment. They can make whatever nonroutine tests and measurements are necessary to ensure that the monitors continue to perform adequately. They can also instruct other agency personnel concerning the proper way to replace filters, detectors, and battery packs, to operate the unit; and to perform field span checks.

Only those persons assigned responsibility for the instruments should make any routine repairs other than the replacement of detectors, photoionization lamps, battery packs and particulate filters, which can be replaced by the inspector and the replacements noted in a log or report provided to the person who has been assigned responsibility for the unit. This reduces the chance of the intrinsic safety of an instrument being inadvertently bypassed by an unqualified individual. The instruments should be returned to the manufacturers for any nonroutine repairs.

Records should be maintained on each instrument including all routine calibrations, any response factor determinations, and all repair notes. Problems reported by field personnel should be briefly summarized in a chronological record. The file should contain at least one copy of each operating manual and a list of all part numbers (if not included in the manual).

4.5 COSTS

4.5.1 Instruments and Accessories

Cost data for various organic vapor analyzers and other instruments have been compiled to illustrate the capital and operating costs. These data are presented simply to help regulatory agencies prepare realistic budgets. They should not be used for comparison of different instruments, as each instrument has different applications and capabilities.

The cost data are based on verbal quotes and published price lists prepared by instrument manufacturers. The data were obtained in December 1985

and were confirmed in January 1986. Cost data presented in earlier reports[24,25,26] are generally out-of-date. All of the price information presented in this section should be confirmed because price increases are expected in the near future.

Also included are the costs of various accessories believed to be helpful in ensuring high-quality field data and acceptable instrument availability. Organic vapor analyzers require numerous accessories and spare parts and the cost of these should be included in the original budgets.

The yearly operating cost estimates presented herein are based on the use of the instrument for 50 days a year, 6 hours a day. It has been assumed that laboratory calibration will be performed before any field work begins and that field span checks will be performed at least twice a day. Costs of calibration gases for the field span checks are based on the disposable-type cylinders offered by several different suppliers.

The cost of the HNU PI-101, the Foxboro OVA 108, and the Bacharach TLV Sniffers are presented in Tables 8, 9, and 10, respectively. The specified costs apply to the intrinsically safe model, which is the only type that regulatory agencies should use. The tables represent the kind of information that should be compiled regardless of which type of instrument or model is being considered.

The relatively large fraction of the basic analyzer cost represented by the accessories reflects the high cost of spare battery packs and rechargers needed because of the vulnerability of intrinsically safe battery packs when not cared for properly. When a battery pack fails, getting a replacement could take anywhere from 1 week to several months; therefore, having spare battery packs and chargers is a necessary expense.

Another major component that drives the accessory costs up is the detector cells. The detector in each of the instruments has one or more sensitive components. Exposure to high temperature, moisture, particulates, or very high organic vapor concentrations can cause premature failure. Regulatory agencies that use these instruments for a variety of purposes ranging from leak surveys to roof monitor emission surveys are likely to damage the detectors occasionally regardless of how carefully the inspectors conduct the field work.

TABLE 8. ESTIMATED COSTS OF HNU MODEL PI-101 PHOTOIONIZATION ANALYZER

Equipment and supplies	Cost, $[a]
Analyzer, Model 81-IS-101-100 (intrinsically safe), with corrosion-resistant detector chamber	5245
Accessories[b]	
Spare 10.2 eV lamp	300
Span gas cylinder regulator	99
Instrument carrying case	250
Spare battery pack	200
Spare recharger	360
Spare probe extension	30
Spare fan	240
Subtotal	1479
	Cost/year, $
Expendable supplies	
Calibration gas cylinder (3 cylinders per year minimum)	150
Particulate filters	20
Cleaning compound ($24 per unit, 1 unit required)	25
Replacement lamp	300
Yearly factory service	300[c]
Subtotal	795

[a] All cost data provided by HNU Systems, Inc.[27,28]

[b] Necessary accessories and supplies specified by Richards Engineering.

[c] Does not include $40 shipping charges.

TABLE 9. ESTIMATED COSTS FOR FOXBORO MODEL 108 FID TYPE ORGANIC VAPOR ANALYZER[a]

Equipment and supplies	Cost, $
Analyzer, with GC option	5200
Accessories[b]	
Spare battery pack	460
Spare recharger	427
Spare probe	40
Recorder (intrinsically safe)	460
Ignitors	32
Pump valves (package of 10)	15
Pump diaphragm	20
Mixer/burner assemblies	200
Washers, TEFLON (package of 12)	18
Washers, brass (package of 12)	15
Calibration kit regulator and case	90
Subtotal	1777
	Cost/year, $
Service and supplies	
Yearly factory service	110[c]
Chart paper ($60/6 rolls, 6 rolls/year)	60
Flame arrestors (package of 10)	9
Calibration gas for field span checks (4 at $63)	252
Factor determinations (2 cylinders at $82 each)	164
Hydrogen gas (< 0.5 ppm HC)	60
Subtotal	736

[a]Instrument related cost data provided by Foxboro.[29] Calibration gas and hydrogen gas cost data.[30,31,32]

[b]Necessary accessories and supplies specified by Richards Engineering.

[c]Does not include $40 shipping charges.

TABLE 10. ESTIMATED COSTS FOR BACHARACH TLV SNIFFER[a]

Equipment and supplies	Cost, $
Analyzer, Model 53-7-TLV	1580
Accessories[b]	
In-line filter and water trap assembly	62
Battery charger	56
Spare battery pack	392
Spare detector cell	115
Calibration kit (regulator, case and 2 cylinders)	212
Subtotal	837
	Cost/year, $
Service and supplies[b]	
Factory servicing	100[c]
Calibration gas for field span checks (4 at $63)	252
Calibration gases for office calibrations and response factor checks (2 cylinders at $73)	146
Replacement detector	115
Subtotal	613

[a]Instrument related cost data provided by Bacharach, Inc.[33] Calibration gas data.[30,31,32]

[b]Necessary accessories and supplies specified by Richards Engineering.

[c]Does not include $40 shipping charges.

TABLE 11. ESTIMATED COSTS FOR OMEGA PORTABLE THERMOMETER[a]

Equipment and supplies		Cost, $
Analyzer, Model 871		225.00
Accessories[b]		
Beaded probes, 6 feet (2 probes)		51.20
Carrying case		10.00
	Subtotal	61.20
		Cost/year, $
Service and supplies[b]		
Replacement batteries (5 at $3 each)		15.00
Calibration (semiannual at $50 each)		100.00
	Subtotal	115.00

[a]Cost data provided by Omega Engineering, Inc.[34]

[b]Necessary accessories and supplies specified by Richards Engineering.

The yearly operating cost of each instrument includes a fee for factory service. This is considered a desirable precaution because the instruments are used for compliance determination and because only limited repair/adjustment of intrinsically safe instruments should be attempted by agency personnel.

One of the main yearly operating costs is for calibration gases (certified to plus or minus 2%) shipped in disposable cylinders. Assuming each field span check requires 1 to 2 minutes and the instrument draws 2 liters per minute, the average disposable cylinder will be adequate for only 10 to 20 measurements (assuming 40 liters of compressed gas). At a rate of approximately $70 per replacement cylinder[30,31,32] each span check would cost between $3.50 and $7.00. Although that is not a high price to ensure high-quality data, some agencies may wish to investigate less expensive alternatives. One alternative is a gas-transfer system. With this approach, calibration gas would be supplied by the same large cylinder used for the laboratory

calibrations and be transported by means of a standard sampling cylinder. The total cost of the components of the sample cylinder system would be $300 to $500.[30,35] This includes a 1-liter, high-pressure, stainless steel sampling cylinder with needle valves, a 10-liter TEDLAR bag, a carrying case, and a regulator. The uncertainty in the cost estimate is due to the lack of available cost data concerning regulators to transfer gas from a large cylinder to a sample cylinder. With the sample cylinder approach, the cost of the calibration gas itself is essentially negligible because sufficient gas would be available from the main laboratory cylinder, which should be purchased once a year. Whereas the initial cost is moderately high, the yearly cost is quite low because the cost of disposable cylinders is eliminated. Another advantage is that the sampling cylinder would only have to be pressurized to approximately 325 psig to provide adequate gas for two span checks per day. This is lower than the 1000 psig used in some types of disposable cylinders. Additional work is necessary to determine if the transfer approach is a safe and economical alternative to the use of disposable cylinders.

The costs of the thermocouple thermometer, shown in Table 11, include the cost of semiannual recalibration against NBS-traceable thermocouples. Although this is a relatively simple procedure, it is assumed that regulatory agencies will not be equipped to perform this calibration. Therefore, the cost for outside calibration has been listed.

The cost of static pressure gauges ranges from $25 to $50 apiece, depending on the range of the unit and the manufacturer. Although no accessories or supplies are generally necessary to maintain these instruments, some attrition of the units can be expected if they are treated especially roughly.

4.5.2 General Equipment

Certain basic equipment is necessary to support the instruments used for inspections of VOC and air toxics sources. The cost for this equipment is presented in Table 12. All of the equipment is used and stored in an instrument laboratory or an instrument shop. The general laboratory equipment is used primarily for calibration of the organic vapor analyzers and for the routine determination of instrument-specific response factors.

TABLE 12. GENERAL EQUIPMENT COSTS

Item	Quantity	Cost/unit, $	Total cost, $	Reference
20-liter TEDLAR bags	2	22	44	35
Bag evacuation pump	1	250	250	35
Cylinder gas regulators	2	198	396	30
Rotameters, stainless steel with needle valve and baseplate	2	123	246	36
Soap bubble flow meter	1	80	80	
Cylinder brackets	2	27	54	30
TOTAL			1070	

4.6 PREPARING BID SPECIFICATIONS

Each type of organic vapor analyzer and thermometer is produced by several different manufacturers. Many of the instrument models offered by the manufacturers come with different options that are tailored to certain applications. Because of the diversity of commercially available instruments, the bid specifications must be prepared carefully.

An instrument that is to be used for VOC leak surveys must meet the EPA Reference Method 21 specifications summarized earlier in Section 3 and presented in Appendix A. An important performance criterion specified is that the readability of the meter scale must be to plus or minus 5 percent of the leak definition concentration, which is 10,000 ppmv in certain industries. To reach this concentration, some instruments must include a dilution assembly. Another important criterion is that the instrument be intrinsically safe for Class I, Division 1 and 2 environments. If a recorder is specified, it also should be intrinsically safe (some are not).

The specific organic chemicals that will be monitored should be identified before bids are solicited. Instruments have considerably different capabilities, and only those with reasonable response factors for the specific chemicals of interest should be used.

The list of accessories and spare parts should be used along with information supplied by the manufacturers on spare parts to determine those that are necessary. Including these items on the bid list will facilitate a more complete evaluation of the total cost of the different instruments.

SECTION 5

INSTRUMENT CALIBRATION AND EVALUATION

Instruments used to determine compliance of industrial facilities must be accurately calibrated on a routine basis. The calibration precision tests, response time, and response factor tests also should be performed to confirm that the instruments are operating properly for the specific application(s). This section presents various calibration and instrument evaluation options available to regulatory agencies that are establishing an instrument program for VOC and air toxics sources.

5.1 INSTRUMENT CALIBRATION REQUIREMENTS AND PROCEDURES

5.1.1 VOC Analyzers

Calibration Procedures--

Calibration requirements for VOC instrumentation are specified in EPA Method 21 and in the specific NSPS applicable to sources of fugitive VOC emissions. The requirements pertaining to calibration are briefly summarized here, and the complete Method 21 regulations are presented in Appendix A.

- The instruments should be calibrated daily.
- The gas concentration used for calibration should be close to the leak definition concentration.
- The calibrant gas should be either methane or hexane.
- A calibration precision test should be conducted every month.
- If gas blending is used to prepare gas standards, it should provide a known concentration with an accuracy of $\pm$ 2 percent.

The daily calibration requirement specified in Method 21 and in the various NSPS gives individual instrument operators some flexibility. The calibration could consist of a multipoint calibration in the lab, or it could be a single-point "span check."[37]

Neither Method 21 nor the applicable NSPS specifies where the calibration takes place. Obviously it would be simpler to conduct the calibration test in the agency laboratory rather than after arrival at the plant being inspected; however, the calibration could conceivably shift sufficiently to affect the accuracy of the leak detection measurements. The degree of possible shift has not been documented for the various commercially available instruments. Although a survey of several major instrument manufacturers indicated that most believe that the units are "calibration stable,"[19,21,38,39] no distinct study has been conducted to demonstrate confidence in the calibration after the instrument has been subjected to vibration during transit. Because of the suspected potential for calibration shifts in all of the organic vapor analyzer types, one should consider conducting at least a single-point span check after the instrument arrives onsite. This concern is shared by several consultants,[16,17] an EPA engineer involved in the development of Method 21[37] and by a number of instrument manufacturers' representatives.[19,38,40] Chehaske has recommended that a span test be run at a midpoint of the day and at the conclusion of the field work.[16]

Although the span checks discussed above would in most cases qualify as the daily calibrations required by the NSPS; a separate calibration test for organic vapor analyzers should be conducted whenever possible. Calibrations performed in the regulatory agency laboratory as compared to calibrations that are conducted in the field are conducted under more controlled conditions because uniform day-to-day calibration gas temperatures and calibration gas flow rates can be maintained in the laboratory.[17] Furthermore, the initial calibration test provides an excellent opportunity to confirm that the entire instrument system is working properly before it is taken into the field. The laboratory calibration data should be carefully recorded in the instrument calibration/maintenance notebook discussed in Section 4, and this calibration should be considered as the official calibration required by the regulations.

The laboratory calibration is best performed by the personnel assigned primary responsibility for the maintenance and testing of all the agency organic vapor analyzers. This ensures the use of proper and consistent procedures. If instrument problems are identified, the instrument can either be repaired or the field inspector can be issued another unit that is operating properly.

Laboratory Calibrations--

As specified in the EPA-promulgated NSPS, the instruments used in accordance with Method 21 must be calibrated by using either methane or hexane at concentrations that are close to the leak-detection limits. In most cases, the leak-detection limit is 10,000 ppmv, however, for certain sources, it is 500 ppmv above the background levels.

Methane-in-air is generally the preferred calibrant gas for the high concentration range.[41] A hexane-in-air concentration of 10,000 ppmv should not be prepared because it is too close to the lower explosive limit. Also, some hexane can condense on the calibration bag surfaces at this high concentration.[11] If hexane-in-air calibrations are necessary, the chosen concentration should be a compromise between the need for adequate calibration of leak-detection levels and the practical safety and reproducibility problems inherent in the use of hexane. The EPA has taken the position that the choice of calibrant gas does not affect the ability of instruments to detect fugitive leaks.[41]

Some VOC instruments, such as photoionization and infrared instruments, do not respond to methane (Section 3). With these units, a different calibration gas should be used. If the inspection is concerned primarily with one specific organic compound (e.g., hexane), that compound can be used for calibration. In other cases, a calibration gas that adequately represents the expected mixture of organic compounds that could be leaking from the source should be used. The calibration gases recommended by the instrument manufacturers are shown in Table 13 as a general guide to inspectors.

TABLE 13. RECOMMENDED CALIBRATION GASES FOR ROUTINE INSTRUMENT SERVICE

Type of instrument	Manufacturer	Calibration gas	Reference
FID	Foxboro	Methane	19
FID	HNU Systems, Inc.	Benzene	20
PID	AID Inc.	Benzene	38
Catalytic combustion	Bacharach	Hexane	43

The calibration procedures for each instrument model are specified in the instruction manuals. Material presented in this section is intended to emphasize the importance of certain calibration procedures discussed in these various instruction manuals.

Regardless of the type of VOC instrument, the flow rate of the gas during calibration should be approximately equal to the flow rate during normal use of the instrument, as flow rate influences the measured concentration.[24] Proper flow rate is very important for the FID instruments.

The two main calibration techniques that can be used are 1) commercially prepared calibration gas mixtures or 2) blended calibration gas mixtures. The commercially prepared calibration mixtures are more convenient, but they are slightly more expensive than the calibration mixtures blended onsite. When commercially prepared mixtures are used, a large cylinder containing a certified concentration of calibration gas (balance of gas mixture is air) is used to fill a TEDLAR bag. The instrument simply withdraws a gas sample from the bag at a rate of 0.5 to 3.0 liters a minute, depending on the normal sampling rate. The estimated time required for the calibration is shown in Table 14.

TABLE 14. CALIBRATION TIME REQUIREMENTS WHEN USING COMMERCIALLY PREPARED CALIBRATION GASES

Activity	Time required, minutes
Set up instrument	2
Instrument warmup and calibration assembly setup	10
Flush sample bags	5
Fill bags with calibration gas and with zero air	2
Reset instrument	5
Record results in notebook or on logsheet	2
Total	26

Obtaining the desired calibration gas mixture in commercially prepared cylinders is sometimes impractical. In such cases, the mixture can be prepared by blending the calibration compound with hydrocarbon-free air in a large TEDLAR or TEFLON bag. This is a much more time-consuming procedure.

For example, the specific steps in the procedures used by Menzies and Fasano[8] are as follows:

1. Flush and evacuate bag three times with hydrocarbon-free air.
2. Fill bag with hydrocarbon-free air.
3. Inject a known volume of test compound into the bag.
4. Permit at least 1 hour of equilibration to ensure adequate evaporation (if sample is liquid) and mixing.
5. Draw gas sample from the bag.

Menzies and Fasano prepared the hydrocarbon-free air by passing compressed air through silica gel (for air drying), charcoal, and a high efficiency filter. As long as the charcoal bed is not saturated with water and/or organic vapor, it should adequately remove organic vapor. Charcoal beds do not remove methane, however. Menzies and Fasano metered the hydrocarbon-free air into the bag by using a rotameter. Presumably, they used precision rotameters or other accurate gas flow monitors to achieve a known concentration within the required accuracy of $\pm$ 2 percent. They injected the calibration compound (a liquid in their work) into the bag with a microliter syringe.

Calibration time requirements can be high. Menzies and Fasano recommended an equilibration time of 1 hour to inject the liquid into the gas. Even when a calibration gas is introduced into a bag, the equilibration time should be between 15 and 30 minutes. Additional time is required to flush the bags several times with VOC-free air. Time requirements for a bag sample calibration are summarized in Table 15.

Because of the lengthy calibration time required by this approach, it would be especially helpful to have an instrument specialist conduct the procedure. This person could calibrate several instruments simultaneously, as much of the time is spent in 1) waiting for the instrument to warmup, 2) waiting for the bag evacuation pump to empty the TEDLAR bag, and 3) waiting for the gas sample to equilibrate in the bag.

When charcoal beds are used to provide the VOC-free air, a routine check should be made to determine breakthrough of organic compounds.[24] This is done by passing a low-hydrocarbon-concentration gas stream (approximately 10 to 50 ppmv) through the bed for a period of 5 to 10 minutes. If the bed has not

TABLE 15. CALIBRATION TIME REQUIREMENTS WHEN CALIBRATION GAS MIXTURES ARE BLENDED

Activity	Time required, minutes
Setup instrument	2
Instrument warmup and calibration assembly setup	15
Empty and flush bags	10
Inject calibration compound and equilibrate	30 to 60
Set calibration and zero	5
Record results in notebook or on logsheet	2
Total	75 to 105

become saturated, the outlet hydrocarbon concentration should be low. Obviously, methane should not be used as the hydrocarbon because charcoal is ineffective in adsorbing methane.

Field Span Check Procedures--

The following are some of the various ways to calibrate the portable instrument onsite:

- Use large pressurized gas cylinders transported to inspection sites.
- Use certified gas cylinders provided by the source being inspected.
- Use disposable gas cylinders with the appropriate gas composition and concentration.
- Use a gas sampling cylinder with a gas blending system.

Transporting large pressurized gas cylinders is generally impracticable because most agencies do not have the vehicles necessary for this purpose. It is not safe to transport unsecured, pressurized gas cylinders in personal or State-owned cars. Furthermore, there are specific Department of Transportation (DOT) regulatons governing the shipping of compressed gases.

Using the source's gas cylinders is certainly the least expensive approach for a regulatory agency; however, the appropriate gas cylinders are not always available. Also, the use of the source's cylinders prevents the agency from

making a completely independent assessment of the VOC fugitive leaks and from evaluating the adequacy of the plant's leak-detection program.

Using disposable cylinders of certified calibration gas mixtures is relatively simple because no onsite blending is necessary and the cylinders are easily transported. The calibration gas mixture may be fed to the instrument directly by using a preset regulator that provides constant gas flow and pressure; or the gas can be fed into a TEDLAR or TEFLON bag, from which it is drawn into the portable instrument.

A third approach involves the use of a stainless steel gas sample cylinder with a small TEDLAR sample bag. A small quantity of calibration gas is drawn from a large cylinder of certified gas mixture (at the agency's main laboratory) into the small transportable gas sample cylinder. The calibration gas is kept at a relatively low pressure to minimize safety problems during transport of the material to the jobsite. The compressed gas is transferred to the TEDLAR bag through a regulator and needle valve. At a pressure of 325 psig, a 1 liter sample cylinder should provide enough span check gas for two field checks. Zero air can be supplied by drawing ambient air through a small charcoal filter. This approach is very inexpensive because the agency is using small quantities of the certified calibration gas mixture from the main cylinder at the laboratory and they are not purchasing any disposable cylinders. Some additional development work on this simple approach is necessary to ensure that a regulator is available to transfer the gas from the main cylinder to the sample cylinder at pressures reaching several hundred psig. Most regulators have a delivery pressure limit of 100 psig.[30,31] It is also necessary to confirm that the compressed gas can be transferred safely. It should be noted, however, that this is the same approach used to fill the hydrogen fuel cylinders on the flame ionization analyzers. Therefore, an approach of this type should be feasible.

Relatively little time is required for the span checks when portable cylinders of certified gas mixtures or transfer gas sample cylinders are used. The time required for various activities is indicated in Table 16. It should be noted that the instrument warmup must be done anyway, therefore this time should not be "charged" against the span check. The overall time commitment to the field span checks is not excessive when one considers the clear indication of organic vapor analyzer performance that these checks provide.

TABLE 16. TIME REQUIRED FOR FIELD SPAN CHECKS

Activity	Time required, minutes
Initial span check	
Assemble and leak-check instrument	4
Warmup instrument and assembly of span check equipment	10
Monitor span check gas	2
Record results in field notes	2
Subtotal	18
Midday span check	
Return to location of span check assembly	15
Fill bag/start span check system	4
Monitor span check gas	2
Record results in field notes	2
Subtotal	23
Final span check	
Fill bag/start span check	4
Monitor span check gas	2
Record results in field notes	2
Empty bag and pack span check equipment	4
Subtotal	12

The field span check should be performed as far away as possible from potential sources of fugitive VOC. It should also be performed in areas where there are no large AC motors or other equipment that generate strong electrical fields, as such equipment can have an adverse effect on certain types of instruments (e.g., photoionization analyzers).[19] The charcoal filter used in the "clean air" supply should be routinely regenerated to avoid the possibility of saturation. The charcoal filter should be checked occasionally for saturation by supplying a moderate, known concentration of VOC and then checking the measured exit concentration after several minutes.

Data concerning the span checks should be recorded in the inspector's field notes. This will demonstrate that the specific unit operated properly during the period in which compliance information was obtained at the

inspection site. If gauges are provided with the instrument, the field inspector also should occasionally note the instrument sample gas flow rate.

5.1.2 Thermocouples

Thermocouples may be tested in several ways. The simplest method for testing is checking a thermocouple in an ice bath and in boiling distilled water. There are electronic "ice point" reference circuits commercially available to check thermocouple operation. There also is an isothermal zone box test equipment to test the thermocouple in a different range. There are several suggestions for thermocouple operation. These include:[3]

1. Use the largest wire possible that will not shunt heat away from the measurement area
2. Avoid mechanical stress and vibration that could strain the wires
3. Avoid steep temperature gradients
4. Use the thermocouple wire well within its temperature rating
5. Use the proper sheathing materials in hostile environments.

5.2 ROUTINE LABORATORY EVALUATION OF INSTRUMENT PERFORMANCE

Routine laboratory evaluation of instrument performance must be conducted. This evaluation includes determination of response factors, determination of response time, determination of instrument sample flow rates, and calibration precision tests.

5.2.1 Determination of Response Factors

When published response factors for the organic compounds being monitored are much greater than 1 (approaching 10) or much smaller than 1 (approaching 0.1), however, it would be prudent to measure the response factor for these specific compounds. A response factor of 10 is the maximum allowed by Method 21, which means that the meter response was 10,000 ppmv when the actual concentration was 100,000 ppmv. Although Method 21 does not specify a lower limit to the response factor, a response factor value of 0.1 means the observed concentration is 10,000 ppmv when the actual concentration is only 1,000 ppmv. The general procedure for measuring the response factor is presented in Method 21 (Appendix A).

5.2.2 Determination of Response Time

The response time of the organic vapor analyzer is an important operating variable. A decrease in instrument response time due either to leakage downstream of the pump or to increased flow resistance through instrument probes and filters can slow down the field work.

For compliance with Method 21 specifications, the response time should be checked before initially using the instruments in the field and whenever the sample flow system has been changed. Agency personnel should conduct this test more frequently, however, to confirm that no leakage of sample air has occurred downstream of the pump. The use of soap solution is the only alternative to identify sample gas leakage after the instrument pump,[18] and it is difficult to apply and observe soap solution in the cramped areas around the instrument pumps. Instructions for conducting response factor tests are included in Section 4.4.3 of Method 21.

5.2.3 Determination of Instrument Sample Flow Rate

For organic vapor analyzers, especially those without flow monitors, the sample flow rate should be measured on a routine schedule. A calibrated rotameter or other flow sensor should be used to determine the flow rate when the typical particulate filters, prefilters, and other flow restrictions are in place. If an instrument rotameter is used, its adequacy should be checked.

The fact that instrument response is relatively insensitive to sample flow rate (i.e., photoionization analyzers) does not eliminate concern over proper flow rate. The tip of the sensor probe operates much like a small hood, and reductions in sample flow rate reduce the effectiveness of pollutant capture. Furthermore, if the probe is not oriented correctly, the "high" pressure organic vapor plume acts like a strong cross-draft across the probe inlet. For these reasons, maximum capture effectiveness is essential, and reduced sample flow rates should be of concern regardless of the type of organic vapor analyzer used.

5.2.4 Calibration Precision Tests

Calibration precision tests must be made before the analyzer is placed in operation and at 3-month intervals thereafter. The general procedures are discussed in Section 4.4.2 of Method 21. As with the other instrument

evaluation procedures, this test is best performed by instrument specialists who are assigned responsibility for routine calibration and maintenance of all the agency's portable instruments (discussed in Section 4.4 of this manual).

5.3 ROUTINE FIELD-ORIENTED EVALUATIONS OF INSTRUMENT CONDITIONS AND PERFORMANCE

Several instrument performance checks should be made before the inspector leaves for the jobsite and during the routine screening of possible fugitive VOC sources. The field-check procedures are in addition to, not a replacement for, the calibration procedures discussed earlier. The daily calibration, the field span checks, and the routine field performance checks are necessary to confirm that the instrument is operating properly. Preferably, the initial instrument checks should be made by the regulatory agency's instrument specialist assigned responsibility for the monitors. Brief notes concerning each day's initial instrument checks should be included in the main instrument evaluation/maintenance notebook kept in the instrument laboratory. The inspectors make the field checks by using the instruments at the jobsite and documentation of these field checks should be part of the inspectors' field notes.

5.3.1 Initial Instrument Checks

It is very important that a few simple instrument checks be made before the inspector leaves for the jobsite. The appropriate field checks for each instrument can be found in the instruction manual supplied by the instrument manufacturer. The following common factors, however, should be checked regardless of the type of instrument:

- Leak checks including integrity of sample line and adequacy of pump operation
- Probe condition
- Battery pack status
- Detector condition
- Spare parts and supplies.

All of these checks can be made in a period of 5 to 15 minutes. Repairs to the detectors, batteries, and probes usually can be accomplished quickly if

a set of spare parts is kept on hand. Some of the checks that should be made before field work is begun are discussed in the following subsections.

Leak Checks--

To leak check the probes on units with flow meters, the probe outlet should be plugged for 1 to 2 seconds while the sample pump is running. If the sample flow rate drops to zero, there are no significant leaks in the entire sampling line. If any detectable sample flow rate is noted, further leak checks will be necessary to prevent dilution of the VOC sample gas during screening tests. The leak checks involve a step-by-step disassembly of the probe/sample line starting at the probe inlet and working back toward the instrument. At each step, the probe/sample line is briefly plugged to determine if inleakage is still occurring at an upstream location. Once the site of leakage has been determined, the probe/sample line is repaired and reassembled. To confirm that the probe/sample line is now free of air infiltration, the probe is again briefly plugged at the inlet to demonstrate that the sample flow rate drops to zero.

When leaks are detected, there is sometimes a tendency to overtighten the fittings, especially those between the instrument body and the end of the sample line. With some types of fittings (e.g., Swagelok fittings) over tightening can damage the fitting and even lead to persistent leaks.[38]

Units that do not have flow monitors should be leak-tested by installing a rotameter on the sample line as close as possible to the inlet to the instrument body. The leak-testing procedure described above can then be followed. Also, the sound of the pump should be noted, as this provides one qualitative means of identifying pluggage. It should be noted, however, that pump noise is useless for identification of probe leakage because the pump continues to receive air due to the infiltration.

One report states that the catalytic combustion units should not be leak-tested by plugging the probe.[24] Short-term loss of sample flow would reportedly lead to high detector temperatures. One manufacturer, however, reports that the detector used on their instrument is the same as the detector used on a diffusion-controlled sampler and that the short-term loss of sample flow would not be a significant problem.[21]

When more than one probe can be attached to the instrument body, each probe should be tested. Only those that can be sealed properly should be packed for field use.

Probe Condition--

The probes for some instruments can contain a number of independent components, especially those that dilute the sample before analysis. The physical condition of the probe should be visually-checked before use. These checks include, but are not limited to:

- Presence of any organic deposits on the inside of the probe
- Presence of clean particulate filter in the probe
- Condition of orifice(s) used to control dilution air flow into the sample probe
- Condition of sealing "O" ring or other sealing assembly used to prevent inadvertent dilution of sample flow.

Any deposits found should be removed, or a different probe should be used. Cleaning instructions can be found in the manufacturers' operating manuals. Generally, the probes are cleaned with acetone and then carefully purged of any acetone vapor before assembly.[19]

Battery Pack Status Checks--

Checking the battery pack is particularly important because it can be a source of frequent problems. The battery pack condition is normally checked by simply switching the instrument to the "Battery Check" position and observing the dial setting. If the battery appears at all weak, a new battery pack should be installed. Most batteries fail because they have not been recharged sufficiently.

The Ni-Cd batteries, used in many photoionization, catalytic, and infrared instruments, must be charged for 8 to 12 hours for each 8 hours of operation. These batteries are very vulnerable to overcharging. Recent improvements in the Ni-Cd battery chargers, however, have substantially reduced the chance of overcharging.[38] Despite a common misconception, the lead acid-gel batteries commonly used in FID instruments are not subject to overcharging, and they should be left on the battery pack recharger whenever the instrument is not in use.[19]

During cold weather, weak batteries will operate for only a short period. In fact, if the unit is to be operated in cold conditions for most of the inspection day, it would be helpful to bring a second battery pack along so the battery pack can be replaced at midday.[19]

Detector Condition--

Each of the instruments includes a key component within the VOC detector. Rather than an initial calibration (recommended earlier in Section 5.1), some inspectors check the detector status by briefly monitoring automobile exhaust. This is not generally advisable because condensable organic compounds and particulate matter can deposit in the probe, partially plug the filters, and even damage the detector. If a qualitative response test is desired, an organic vapor source, such as a cigarette lighter (do not take into plants to be inspected), certain marking implements, liquid paper thinner, or a small sample bag should be used. A complete calibration is preferred over these qualitative response checks.

The flame ionization instruments are checked by depressing the ignitor button for several seconds. If the unit will not ignite after repeated attempts, there may be problems with the batteries, ignitor, or hydrogen supply. Most of these problems cannot be solved immediately; therefore, other instruments will have to be used until the repairs are completed. Hydrogen leak problems are much less prevalent with newer instruments.[19] Failure of the catalytic units to respond to organic vapor is often due to failure of the main detector cell, an easily replaced component.

Spare Parts and Supplies--

Most of the instruments used on VOC inspections are sophisticated instruments rather than simple "off-the-shelf" items. Each requires some spare parts and supplies to ensure that the inspection is not terminated prematurely. Table 17 provides a partial listing of the recommended spare parts for each general type of instrument. All of the parts listed should be carried to the jobsite. Other spare parts (discussed in Section 4) should be left at the instrument laboratory/shop. Further information is available in the manufacturers' operating manuals and from the manufacturers' representatives.

TABLE 17. PARTIAL LISTING OF RECOMMENDED ONSITE SPARE PARTS AND SUPPLIES FOR PORTABLE INSTRUMENTS

Instrument	Spare parts and supplies
Flame ionization detectors	Battery pack Particulate filters Glass wool TYGON tubing (1 foot)
Photoionization detectors	Window cleaning kit Spare lamp Particulate filters Glass wool Dilution probe TYGON tubing (1 foot) Rotameter Battery pack
Nondispersive infrared detectors	Battery pack Particulate filter Rotameter Glass wool TYGON tubing (1 foot)
Catalytic combustion units	Detector Battery pack Particulate filter Rotameter TYGON tubing (1 foot)
Thermocouples	Battery Probe

5.3.2 Routine Performance Checks During Field Work

Several routine performance checks should be conducted during field work. These checks take very little time and demonstrate that the unit is continuing to perform in a proper manner. They also should be discussed briefly in the field notes.

Instrument Zero--

The instrument zero should be rechecked whenever it has been exposed to very high organic vapor concentrations and whenever organic liquids may have been inadvertently sucked into the probe.[18,24,44] The instrument zero should be checked at least twice a day, even when these problems do not occur or are

not suspected. It can be checked by sampling background air at a location upwind of any possible VOC sources or by supplying some charcoal-filtered air to the analyzer. If the zero has drifted significantly, the probe particulate filter and the prefilter (if one is used) should be replaced. Also, the probe should either be cleaned or replaced. The instrument then should be recalibrated before the field work continues.

Instrument Response--

The instrument response should also be checked routinely during field testing because all of the instrument types are vulnerable to operating problems that can result in reduced sensitivity or complete loss of response. In the case of FID's, exposure to very high VOC concentrations (above 70,000 ppmv) can lead to flame out of the unit.[19] It is sometimes difficult to hear the audible flame-out alarm over plant noise unless earphones (supplied with some models) are used. If the inspector fails to hear the flame-out alarm, he or she could miss a number of fugitive leaks.

The catalytic combustion units are also vulnerable to problems when exposed to very high concentrations. The detector can reach temperatures high enough to cause some loss of the catalyst coating.[21] If done repeatedly, this can also shorten the life of the detector.[21] Exposure to lead-containing gasoline can lead to some poisoning of the detector catalyst.[21] For these reasons, the response should be checked whenever the unit is "pegged." The remaining gas in the TEDLAR bag used for span checks provides a convenient source of organic vapor to confirm instrument response.

Response problems of the photoionization and nondispersive infrared detectors result primarily from deposition of condensed organic compounds on the optical surface. The window should be cleaned at least once a day and whenever material might have been deposited as a result of exposure to high concentrations or entrained liquids.[39,40,45] Unfortunately, contamination on the optical window is not always visible. Therefore, inspectors should simply assume the window is dirty and take the necessary time to use the cleaning solution. Instrument manufacturers recommend a solvent similar to methanol (instrument manufacturers should be contacted for specific recommendations) for routine cleaning.[39,40] The cleaning compound is mildly abrasive and is intended only for stubborn deposits that cannot be removed by more gentle cleaners.[27]

Battery Condition--

In the case of some FID's, weak batteries will not have enough power to operate the ignitor, even though a proper reading was obtained during the battery check.[19] This can be a problem after the FID has been operated for several hours and after a number of flame-outs have occurred. Therefore, the instrument operator should check the battery condition several times during the day.

Probe/Sampling Line Leakage--

The probe and sampling line integrity should be checked several times a day by simply plugging the probe inlet. The flow rate indicated by the instrument meter (if one is present) and the sound of the instrument should be noted. Any potential leaks should be corrected before work is continued.

SECTION 6

FIELD INSPECTION PROCEDURES AND INSPECTION SAFETY

This section presents field measurement procedures for regulatory agency inspectors. The first subsection presents several basic reasons why the measurement procedures used by agency inspectors are inherently different from those that may be used by source personnel or their consultants. It also presents some important basic principles concerning the inspection of VOC and air toxic sources. The remaining subsections concern major types of sources for which portable inspection instruments have proven useful. Safety considerations have been integrated with the information concerning field inspection procedures and underlined to emphasize their importance as an essential part of all activities involving the portable instruments.

6.1 PRINCIPLES, REQUIREMENTS, AND LIMITATIONS OF AGENCY INSPECTIONS

One of the basic premises of the inspection techniques presented in this section is that the agency inspector does not have sufficient time to survey all potential sources of fugitive emissions independently or to monitor the performance of all air pollution control devices completely. Furthermore, each inspection involves a review of the permits, a review of operating records, and interviews with appropriate plant supervisory personnel. Because the use of portable instruments, the subject of this manual, composes only one part of the overall inspection, it is unrealistic to assume that agency inspectors can spend the majority of the inspection day using the portable instruments. Rather, inspectors must be able to select those few measurement activities that are most useful in the characterization of the overall conditions at the facility. In the case of fugitive VOC and air toxic leaks, the inspector must determine the monitoring accordingly.

Field inspection surveys conducted by plant personnel and consultants often involve a team of at least two individuals--one to operate the instrument and one to record the data and tag the appropriate sources.

Regulatory agencies usually send only one inspector. As a result, the inspection proceeds more slowly, as the inspector normally must set the instrument down to record the results. This problem cannot be solved by the use of continuous recorders because most of them are not intrinsically safe and should not be used.

The data obtained by regulatory agency inspectors must be of the highest quality reasonably possible because these data are used to determine the compliance status of the facility. Time should be allocated for the field span checks, response checks, and zero gas checks discussed in the earlier sections. It is preferable to have a limited set of data of unquestionably high quality than a large set of potentially inaccurate data.

6.1.1 Inspection Principles

Use of the baseline technique is the best approach to inspection of air pollution control devices such as carbon-bed adsorbers, incinerators, and vapor recovery. The baseline technique is based on the comparison of current inspection data against unit-specific performance data obtained in the past. Shifts in several operating parameters are used as an indication of problems. The portable instruments are used only when there are insufficient onsite equipment performance monitors or when reasonable questions arise concerning the adequacy of the onsite gauges. The basic principles of the baseline technique are as follows:

- Only unit-specific data are used to evaluate performance.
- Portable instruments are used when onsite gauges are either unavailable or unreliable.
- Problems are identified by evaluating changes in a number of operating parameters and conditions.
- The information is compiled in a methodical manner.
- The inspection procedure is modified or limited to the extent necessary to ensure safety of the inspector, plant personnel, and the source's equipment.

The baseline technique is not directly applicable to the fugitive VOC and air toxics leak sources, as no directly observable valve or pump operating parameters govern the rate of fugitive emissions. These sources either leak or

they don't. For the fugitive leak sources, the baseline concept should be applied to the plant's leak-detection and repair program rather than to the individual leaking components. The adequacy of the leak-detection procedures is determined by spot-checking potential leaking sources and by rechecking those components that have been tagged previously. Changes over time in the leak-detection and repair program that could have an adverse impact on total emissions should be evaluated. In other words, the adequacy of a plant's leak-detection and repair program is evaluated by using leak data obtained during the current inspection and data obtained during previous inspections. This is a more accurate approach than simply evaluating what activities are conducted at what frequency in a given plant's program. The type of programs necessary at one plant and those at supposedly similar facilities can differ significantly.

6.1.2 General Safety Procedures

All agency personnel should have an occupational health medical examination before conducting any field inspections. This examination demonstrates that the inspector is physically capable of the stress associated with carrying the portable instruments, climbing ladders/stairs, and wearing the required respirators and other personnel protection equipment.[46] Annual medical examinations should be required.

All regulatory agencies should adopt and adhere to written safety procedures governing all routine activities of field personnel.[46] Specific safety procedures concerning the use of portable instruments and the types of industries the inspector will visit should be included in these procedures.

Because agency coworkers are rarely present, the inspector should insist that someone from the plant accompany him or her at all times to ensure that the inspector does not inadvertently enter unsafe areas, to assist the inspector in the event of accidental gas releases within the facility, to get help if the inspector is injured, and to provide general assistance and advice regarding safety.[46,47] Inspectors should not work alone in the facility for any reason.

Prior to leaving for the jobsite, the inspector should obtain all necessary safety equipment. All the safety equipment, especially respirators, should be checked to confirm that they are in good working condition. The proper safety shoes should be worn for the conditions that exist at the facility being

inspected. Because safety shoe requirements differ, the plant should be consulted to determine the proper type of shoe before the inspector departs for the jobsite.

Before entering the processing areas of the facilities, the inspector should discuss the instrument intrinsic safety with the appropriate plant representatives. Portable instruments that are not intrinsically safe should not be taken into Class I, Division 1 and Division 2 areas.

During the field survey, the inspector should use an organic vapor analyzer to help determine if conditions are safe. This is especially true when a tank with a floating roof is only partially full. These situations must be approached with great caution as they are similar to entering a confined area. Half-face cartridge-type respirators for organic vapor are limited to maximum concentrations of 50 ppmv. This concentration can be easily exceeded in the immediate vicinity of fugitive leaks. The inspector should use the organic vapor analyzer to determine if poorly ventilated areas have organic vapor concentrations in the breathing zone that are above the concentration limits of the respirator.

Inspectors rarely have the opportunity to acclimate to heat stress. Heat exhaustion and stroke can result from the physical exertion of carrying the instruments and from exposure to hot process equipment. Inspectors should plan to take regularly scheduled breaks and drink fluids to reduce the risk of heat exhaustion and heat stroke. These breaks are good times to check the zero drift or to perform the field span checks of the portable instruments.

6.2 SCREENING TESTS FOR VOC LEAKS FROM PROCESS EQUIPMENT

The primary purpose of the VOC leak-screening tests is to determine if the plant's leak-detection and maintenance program is adequate. The inspection consists of a review of the leak records and a field survey with an organic vapor analyzer.

6.2.1 Selecting an Inspection Strategy

Because the time available for the field survey is often limited, the most probable "leakers" should be targeted for evaluation. The inspector should consider the following factors to determine potential problem sources.

- Specific components identified as leakers in the past
- Type of service (e.g., gas, light liquid, heavy liquid)

- o Type of component (e.g., valves, pumps, flanges, compressors, open-ended lines, relief valves)
- o Pressure of line
- o Temperature of line
- o Specific design of component (e.g., type of pump seal, type of valve, type of valve packing)
- o Age of equipment/component
- o Volatility of specific organic compound(s) being handled
- o Presence of dripping liquids.

Because the field inspector does not have the luxury of spending hours to determine the optimum field survey strategy, it is recommended that field monitoring primarily emphasize the following: 1) those components/process areas with a demonstrated history of high leak rates, 2) valves in gas and light liquid service, 3) pumps in light liquid service, and 4) compressors. Data obtained during a number of EPA-sponsored studies and private studies have clearly indicated that these sources have the highest frequency of VOC leaks in refineries and synthetic organic chemical manufacturing industry plants.[25,48,49,50] For example, data compiled by Wetherold et al.[51] and shown in Table 18 indicate that valves and pumps in heavy liquid service leak much less frequently than those in gas service and in light liquid service (light liquid means a boiling point below that of kerosene; heavy liquid means a boiling point equal to or above that of kerosene). Investigators have generally concluded that most chemical plant and refinery components in heavy liquid service have a low probability of leaking.

The data presented in Table 18 clearly indicates that flanges are a relatively minor source of emissions. Although this is consistent with other studies of petroleum refineries, the flange leakage in some synthetic organic chemical manufacturing industry facilities may be higher, based on observations by Harvey and Nelson.[49] Nevertheless, flanges are not good targets for the field survey because they are numerous and their overall leak rate is less than those of other components.

Conversely, most refineries and synthetic organic chemical manufacturing industry plants have very few pumps and compressors, but the leak frequencies

TABLE 18. ESTIMATED LEAKAGE RATES FOR REFINERY COMPONENTS[a]

Source type	Estimated percentage that are leaking
Valves	
Gas/vapor streams	29.3
Light liquid/two-phase streams	36.5
Heavy liquid streams	6.7
Flanges	3.1
Pump seals	
Light liquid streams	63.8
Heavy liquid streams	22.8
Compressor seals	
Hydrocarbon service	70.3
Hydrogen service	81.2
Drains	19.2
Relief valves	39.2

[a]Information abstracted from Table 1-1 in Reference 25.

appear to be high. Several of these should be included on the field survey. Any pump that has liquid dripping from the seal certainly should be monitored[52,53] although this is not an entirely reliable indicator of excessive fugitive emissions.[52]

Because of their large number in a typical refinery or synthetic organic chemical manufacturing industry plants, valves are considered dominant sources of fugitive VOC emissions,[25,48,49] and a number of these should certainly be included on any field survey. Unfortunately, the EPA-sponsored studies indicate that a relatively small fraction of the valves are responsible for most of the emissions from this fugitive source. For example, Wetherold and Provost found that 3.6 percent of the valves were causing more than 90 percent of the fugitive emissions attributed to valves.[25] To the extent possible, the inspector should target the field survey toward the offending valves. The identification of the problem is complicated by the fact that a typical refinery could have more than 10,000 to 20,000 valves.[49,54]

Soap solution can be used to help in the selection of the valves to monitor.[47,48,50] The time required to spray the soap on the valve stem, however, is just slightly less than that required to monitor the emissions with an organic vapor analyzer. Soap screening techniques are more appropriate when the actual emissions are to be quantified by source bagging, which is a time-intensive approach. Source bagging is commonly practiced as part of special fugitive leak studies, but it is not a routine inspection tool.

During the field survey, inspectors should listen for any audible leaks, as this may help to locate "leakers" that were not suspected. Sometimes odors also can be of benefit in adjusting the field survey portion of the inspection. The effectiveness of both of these techniques is limited, however.[55]

Another technique of limited usefulness is the "walk through" survey, in which a portable organic vapor analyzer is used to identify areas of high concentrations relative to background concentrations. Supposedly, these areas would be in the immediate area of fugitive leaks. Unfortunately, this technique does not appear to be a reliable indicator of fugitive leak locations. Weber and Mims found that the results could not be reproduced even when the technique was repeated almost immediately.[56]

With regard to line pressure and temperature, Wetherold et al. found no significant relationship between these parameters and leak frequency in refineries,[51] however, Langley et al. found that line pressure did correlate with leak frequency in selected synthetic organic chemical manufacturing industry facilities.[57] Inspectors should consider line pressure only as a secondary variable when attempting to evaluate the most important components and/or process areas.

6.2.2 Measurement Procedures

Fugitive leaks from valves in closed systems occur primarily from the valve stem packing gland. This packing material is intended to seal the process gas and/or liquids from the atmosphere. As the packing lubricant is lost or the packing material wears, some volatilization of organic vapors is possible.

For these types of valves, the emissions are monitored at the point where the valve steam leaves the packing gland. The normal procedure is to circumscribe this location with the probe within 1 centimeter of the valve stem. This close location is necessary because of the relatively poor capture

effectiveness inherent in the probe designs used on commercially available instruments. The capture effectiveness decreases very rapidly with distance from the probe. The presence of a strong cross-draft due to ambient wind further reduces the probe capture capability. For these reasons, the probe must be placed very close to the valve packing gland. It should be noted, however, that this brings the inspector into the immediate vicinity of the leak because of the short length of most probes. While monitoring the leak, the inspector could exceed the safe operating range of the respirator and even saturate the respirator cartridge. To minimize inhalation hazards, the inspector should terminate any screening tests when the concentration of organic vapor in the breathing zone exceeds the maximum safe concentration of his or her specific respirator.

Some EPA-sponsored work has indicated that fugitive emissions from sources such as valves could be reliably monitored at 5 centimeters from the valve stem rather than the 1-centimeter distance discussed above.[52] A leak definition of 1000 ppmv at 5 centimeters appears equivalent to the conventional leak definition of 10,000 ppmv at 1 centimeter. The 5-centimeter distance is an attractive alternative because this lessens the chance that liquids on the surface of the valve will be carried into the instrument. For Method 21 inspections, however, leak definition of 10,000 ppmv at 1 centimeter should be used to ensure consistency with the regulation.

Valves used on the ends of drains or sample lines have two sources of leakage, the valve stem and the valve seat. Most sources use a double valve arrangement or incorporate a blind flange to protect against emission losses through the valve seat of the main shutoff valve. To confirm the adequacy of the drain or sampling line seal, the probe is usually placed at the center of the discharge pipe.

Fugitive emissions from pumps occur from the pump shaft seal used to isolate the process fluid from the atmosphere. The most commoly used seals are single mechanical seals, double mechanical seals, and packed seals. Monitoring is done within 1 centimeter of the seal and the rotating shaft. A rigid probe tip should not be used near the rotating shaft. The probe tip could break if the inspector were not able to hold the probe absolutely steady during the measurement. A flexible tip is usually added to the end of the rigid probe when sampling pumps.[16,58]

Most pump shafts have shaft guards that protect against entrapment in the rapidly rotating shaft. With some instruments, it is difficult to reach through the guard to the location of the shaft and shaft seal. The guard should not be removed under any circumstances, and those pumps without guards should be approached very carefully. If there is any question concerning the safety of the measurement, it should not be performed. Pump monitoring safety should be discussed with plant personnel before the field survey portion of the inspection is initiated.

Several organic vapor analyzer problems can be caused by sampling gases having too high a concentration. At hydrocarbon concentrations above 70,000 ppmv, flame-out of flame ionization detectors can occur.[19] High concentrations of hydrocarbons can lead to very high detector temperatures and the loss of catalyst in catalytic units. Condensation of a portion of these high concentration vapors on photoionization unit lamp windows can reduce the sensitivity of the instrument. The condensation of material in the probe and sampling lines can be a problem for all types of instruments. For these reasons, the inspector should monitor the hydrocarbon concentration while slowly approaching the valve stem, pump shaft seal, or other source. If the instrument gauge indicates high concentrations, the specific leak site on the valve stem or pump seal should be approached very carefully. In some cases, the concentration will exceed the leak definition even before the probe is placed close to the leak site. Obviously, in these cases, there is no need to move the probe closer and risk affecting the performance of the organic vapor analyzer. Furthermore, there is nothing to be gained by maintaining the probe at the leak site for two times the response time (a general rule) if the instrument already indicates a concentration above the leak. To the maximum extent possible, field inspectors should protect the organic vapor analyzers against high organic vapor concentrations.

The organic vapor analyzer probe should never be placed in direct contact with liquids during the monitoring of fugitive emissions. A portion of the liquid could be pulled into the probe and damage the instrument detector. If there is contact with liquid, it may be necessary to clean and/or repair the instrument.

The inspector also must exercise care when monitoring sources, such as valves and pumps, that handle heavy liquid streams at high temperatures. Relatively nonvolatile organic compounds can condense in the probe and the

detector. Both the instrument response to the emissions and the instrument return to zero may be slowed because of the condensation of these compounds. For fugitive VOC sources that have a highly variable leak rate, the maximum sustained concentration or maximum repeated concentration observed should generally be recorded.

Certain fugitive leak sources are subject to a "no detectable leak" regulation, i.e., the difference between the background organic vapor concentration and the concentration downstream of the source should not be greater than 500 ppmv. The background concentration is determined by placing the probe 1 to 2 meters upwind of the source. If other equipment interferes with the background measurement, the upwind monitoring location can be as close as 25 centimeters.

No heroic attempts should be made to reach valves and other fugitive sources in inaccessible locations. A relatively high percentage of the valves are often in difficult-to-reach locations.[55,59]

6.3 INSPECTION OF CARBON-BED ADSORBERS

Carbon-bed adsorbers are used to recover valuable solvents used in the manufacturing process. Most larger systems are regenerative units with two or more carbon-bed vessels. The beds are isolated one by one for regeneration while the others remain on-line. Steam is the most common means of bed regeneration. Selection of the regeneration cycle is based on the need to maximize solvent recovery while minimizing steam consumption. The organic compounds desorbed from the bed during regeneration are condensed, along with the steam, in a condensor. The water and the solvents are then separated in a decanter. Unless the field inspector has a prior background in carbon-bed design and operation, it will be difficult to identify carbon-bed system problems by using only the control device gauges.

Portable inspection instrumentation is very useful for this type of air pollution control device because it provides a direct means of determining whether the removal efficiency has decreased since the baseline period. The effluent gas during the adsorption period from each separate bed should be between 50 and 500 ppmv, if the carbon bed is being operated properly and the adsorbent remains in good condition. If the bed is being operated too long between regeneration cycles or the adsorbent is no longer able to handle the

solvent loading, the effluent gas concentration increases dramatically. Emissions can also increase if the bed has become partially saturated with hard-to-remove compounds.

To determine if the carbon beds have a "breakthrough" condition, the inspector places the portable organic vapor analyzer near the exhaust of each individual bed.[60,61] The emissions should be monitored several times during the adsorption cycle of each bed. Because the instrument usually is not calibrated for the specific solvents being handled, the value does not correspond directly with the actual concentration. Nevertheless, a comparison of the current value against effluent concentrations that were measured when the control system was working properly provides an indication of operating problems. A very high reading during the inspection is also a clear indication of bed problems.

Before being used in field work, the organic vapor analyzer should be calibrated for a moderately low concentration. A calibration to 10,000 ppmv methane is not appropriate when the emissions being measured are expected to be in the range of 50 to 500 ppmv.

Portable instruments generally can be used safely on the exhaust streams because the maximum organic vapor concentration is rarely above 25 to 50 percent of the lower explosive limit (LEL). Nevertheless, field inspectors should use only intrinsically safe instruments as other areas around the carbon bed or the facility could have potentially explosive vapors during unusual operating conditions.

No heroic efforts should be made to monitor carbon-bed exhaust vents that are in difficult to reach locations. These exhausts are often too high to reach with standard probes. Inspectors also must be careful to avoid the downdraft emissions from the vents. Even when the carbon-bed is operating properly, the organic vapor concentrations exceeds the maximum allowable concentration of cartridge-type respirators. When the bed is not operating properly, concentrations in the stack can be very high. Plume downdraft is quite common because the gas stream is not very hot, the exit velocities are low, and the vents are usually only 5 to 15 feet above the ground.

Carbon-bed performance problems identified by the organic vapor instruments can be confirmed by using a solvent material balance. Because it is relatively time-consuming, however, this exercise is generally performed only when the bed

emissions are abnormally high or when safety considerations preclude the use of measurements.

Static pressure gauges have a limited application in the inspection and evaluation of carbon-bed adsorbers. The gauge can be used to measure the static pressure drop across the bed if static pressure measurement taps are available above and below the bed. These data are useful in determining if the bed has collapsed (often caused by corrosion) of if the total gas flow rate to the carbon-bed has increased substantially.

6.4 INSPECTION OF THERMAL AND CATALYTIC INCINERATORS

Theoretically, thermometers should be very valuable for routine inspections of thermal and catalytic incinerators. On all types of incinerators, the operating temperature is one of the main variables determining the effectiveness of pollutant destruction. The independent measurement of the incinerator operating temperature during the inspection would be very useful in confirming proper operation. Unfortunately, however, the incinerators rarely have ports in which a thermocouple could be inserted to determine the temperature, partially because it is very difficult to obtain accurate measurements with portable thermometers. If the probe is placed within the direct line-of-sight of the burner flame, the radiant energy received by the probe can indicate higher-than-actual gas temperatures. Conversely, thermocouple probes partially or completely shielded by refractory baffles can indicate much lower-than-actual gas temperatures. Most facilities rely on permanently mounted temperature indicators installed with the incinerator rather than attempting to measure the incinerator temperature. Chances that an onsite gauge will be significantly in error are slight because failure of the onsite temperature monitor usually causes the incinerator to trip off-line. For these reasons, regulatory agency inspectors generally use the onsite gauge to confirm the proper operation of incinerators.

If an independent temperature measurement is needed, the inspector can monitor the incinerator stack temperature. A drop in this value compared with baseline data indicates a decrease in the incinerator operating temperature. Whereas actual incinerator conditions could not be reliably inferred from the stack temperature data alone, large decreases in the stack temperature could

demonstrate the need for a stack test. Most thermal and catalytic incinerator stacks, however, do not have appropriate ports for portable thermocouples, and many of those that do are in inaccessible locations. Inspectors must be extremely careful when making measurements on incinerator stacks. Potential problems include (but are not limited to) severe burns, heat stress, falls, and inhalation hazards. It should also be noted that battery-powered thermometers are generally not intrinsically safe; therefore, these instruments cannot be used in areas where potentially explosive gas mixtures or dust clouds could exist.

Although specific procedures have not yet been developed, organic vapor analyzers could conceivably be used as part of an incinerator inspection. A portion of the incinerator stack gas could be withdrawn and cooled to a gas temperature compatible with the organic vapor analyzer. Presumably, this would require that the instrument probe be replaced with a sampling train including a high-temperature probe, a condensor, a moisture trap, and a particulate filter arranged in series. The measured organic vapor concentration would provide a direct indication of the effectiveness of the incinerator. Actually, a procedure of this type would be difficult to implement at the present time for the following reasons:

- The sampling train includes several bulky items that are time-consuming to setup and cumbersome to transport.
- A traverse of the stack would be necessary to determine the presence of any stratification of partially combusted organic vapors.
- Condensation of nonvolatile organic compounds could plug the particulate filter or damage the instrument detectors.
- Failure to cool the stack gas adequately would result in damage to the instrument.
- There is no assurance that the instrument will detect a sufficient fraction of the partially combusted organic compounds.

For these reasons, field inspectors do not currently use this technique. All of the sampling train problems probably could be worked out, however, the uncertainty of instrument response due to unknown organic compound species may preclude use of this technique. At the present time, it is recommended that regulatory agency inspectors not attempt to use organic vapor analyzers for the evaluation of incinerator effluent.

6.5 INSPECTION OF VAPOR RECOVERY SYSTEMS

Three major types of vapor recovery systems are commonly used at gasoline terminals: 1) carbon-bed adsorbers with followup gasoline absorption, 2) refrigeration, and 3) thermal oxidation. Portable instruments can be used to a limited extent to inspect these air pollution control systems.

Vapor recovery systems using carbon adsorbers are inspected in a manner similar to that described earlier for carbon-bed adsorbers in Subsection 6.3. If the exhaust vent for each bed (normally there are two beds) is accessible, the organic vapor analyzer probe can be used to confirm that the exhaust concentration during the adsorbtion cycle is less than 500 ppmv. Failure of the desorption process or saturation of the bed both lead to "breakthough" and very high VOC concentrations during the adsorbtion cycle. In fact, the emissions from the carbon bed during severe malfunction can be within the explosive range.

The potentially high vapor concentrations necessitate that the probe initially be placed well downwind of the exhaust vent in an area where dilution of the effluent has already occurred. If the observed concentration is high (> 200 to 300 ppmv), the bed obviously is not operating properly and no further measurements are necessary. If the downwind concentration is very low, the probe can be advanced slowly toward the exhaust vent itself. If the observed concentration exceeds several thousand ppmv at any time, the measurements should be discontinued. This cautious approach is required because of the remote possibility that a significant static charge can accumulate on the instrument probe or the inspector's clothing as he or she walks around the unit. A spark in a cloud of gasoline vapors within the explosive range would have serious consequences. Therefore, the probe is never allowed to enter the exhaust plume at an area where explosive concentrations could conceivably exist.

Many carbon-bed vapor recovery systems do not have platforms above the beds to permit access to the exhaust vents, which are usually 10 to 15 feet above the ground. When this is the case, inspectors should not attempt to climb up to the vapor recovery systems to reach the exhaust vents.

Portable instruments have very little application in the inspection of the refrigeration and incinerator vapor recovery systems. In the case of the

refrigeration units, the normal exhaust concentrations are 30,000 to 50,000 ppmv, which are above the normal operating range of most instruments. Furthermore, the gasoline vapor concentration can be in the explosive range. Also access to the exhaust vents, normally 10 to 15 feet high, is generally very poor. The thermal incinerators rarely have measurement ports to permit the use of portable thermometers, and the inherent measurement accuracy problems are the same as those for large thermal and catalytic systems.

6.6 SURVEYING EMISSIONS FROM STACKS, VENTS, AND ROOF MONITORS

Regulatory agency personnel have expressed an interest in evaluating the organic vapor emissions from stacks, vents, and roof monitors as part of special inspections. Some of the principal objectives of these surveys are summarized below:

- To evaluate possible sources of community odors.
- To evaluate emissions from bypass stacks and vents believed to be sealed.
- To evaluate adequacy of pollutant capture in specific process areas and buildings.
- To identify sources of organic compounds not currently included on the plant emission inventory or covered by operating permits.

These activities are obviously different from those of a conventional source inspection. Unfortunately, most regulatory agencies currently do not have the necessary equipment to perform such evaluations. Presumably, the organic vapor analyzers purchased for inspection of VOC and air toxic sources could be used for these additional activities.

Stacks, vents, and roof monitors are difficult sources to measure with portable organic vapor analyzers. All of the commonly used instruments are easily damaged if particulate is carried into the instrument detector. Condensable organic vapors, condensable acid vapors, and moisture could severely damage the instrument detectors, the instrument pumps, and the entire sample-handling system. Thus, the instruments should include a moisture trap and a particulate filter, at the very minimum. An additional glass wool plug at the probe inlet would provide additional protection. Both the glass wool

and the instrument particulate filter should be changed if there is an indication that the sample flow rate has decreased during the survey.

High organic vapor concentrations can lead to flame-out of the FID's and damage to all types of instrument detectors. When high concentrations are expected, the instrument should include a dilution probe. As an alternative, the sample could be taken in a TEDLAR or TEFLON bag and diluted with hydrocarbon-free air before the instrument is used. If high VOC concentrations are accidently found, the probe should not be left in the high concentration stream for a long time.

In sources of this type, the specific chemical compounds in the gas stream are rarely known. Lack of knowledge concerning the appropriate response factors makes it difficult to interpret the organic vapor analyzer meter readings. The instrument simply provides a qualitative indication of the presence or absence of high concentrations of organic vapors. In some compounds, the response may be so poor that small sources of emissions will not be reliably identified. To improve the reliability of detection, field inspectors could use two different types of analyzers. Combinations such as an FID and a PID, a catalytic unit and a PID, or an FID and an infrared unit would cover a much broader group of organic compounds. This also increases the time and difficulty of the survey, however.

Before conducting any surveys of stacks, vents, and roof monitors, regulatory agency personnel should carefully evaluate the potential safety hazards and the potential variability of emissions. It may be difficult to obtain good data even if the instruments are responding properly.

Many fugitive emissions passing up through the stacks, vents, and roof monitors are intermittent in nature. Some degree of luck is necessary to have the instrument at the right spot at the right time. The probability of detection is improved if the inspector is familiar with the plant operating cycles. Even with a good working knowledge of the plant operations, however, the inspector can miss the short-term emission events. Another major problem is the size of some of the vents and roof monitors. The probes used with the portable instruments are relatively short and would not be appropriate for traversing large open sources. Although the use of longer probes is possible, the additional flow resistance could have a detrimental effect on the

instrument's sample gas flow rate. This is important because some instruments, notably the FID, are especially sensitive to flow rate variation.

Several potentially serious safety problems must be considered before surveys of stacks, vents, and roof monitors are attempted:

- Falls through weak roofs
- Sudden exposure to potentially toxic compounds through inhalation if a pollutant downdraft exists
- Heat stress around hot sources
- Climbing hazards because of the cumbersomeness of the portable instruments and accessories.

The most important of the safety problems is the possibility of falls through weak roofs. Structural problems in portions of roofs are very common and it is often difficult to spot the weak areas. Agency inspectors must exercise extreme caution when walking across or working on roofs. Unfortunately, walking across the roofs is the only way to read most of the vents and roof monitors. The second major problem is the sudden exposure to high concentrations of potentially toxic organic compounds. Exposure can occur before the inspector can put on the respirator and the organic vapor concentrations can greatly exceed the allowable limits of the respirator. The problem is further compounded by the fact that some of the organic compounds are skin- and eye-absorbable, thus limiting the help provided by a respirator.

Based on the potential instrument damage, the uncertainties of instrument response, the variability of pollutant emissions, and the possible safety hazards, extreme care should be exercised in conducting these type of surveys. Obviously, if unsafe conditions exist with respect to these type of surveys they should not be conducted.

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APPENDIX A

REFERENCE METHOD 21 AND NSPS AND NESHAPS REGULATIONS

REFERENCE METHOD 21

Method 21. Determination of Volatile Organic Compounds Leaks [196]

1. Applicability and Principle.

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

2. Definitions.

2.1 Leak Definition Concentration. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

2.2 Reference Compound. The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

2.3 Calibration Gas. The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

2.4 No Detectable Emission. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is not present. Since background VOC concentrations may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than a concentration corresponding to the minimum readability specification indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

2.5 Response Factor. The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

2.6 Calibration Precision. The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

2.7 Response Time. The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

3. Apparatus.

3.1 Monitoring Instrument.

3.1.1 Specifications.

a. The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

b. The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

c. The scale of the instrument meter shall be readable to ±5 percent of the specified leak definition concentration.

d. The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be ½ to 3 liters per minute.

e. The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association). [2 3]

3.1.2 Performance Criteria.

a. The instrument response factors for the individual compounds to be measured must be less than 10.

b. The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

c. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

d. The evaluation procedure for each parameter is given in Section 4.4.

3.1.3 Performance Evaluation Requirements.

a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

3.2 Calibration Gases. The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, less than 10 ppmv VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration gas mixture are used, they must be analyzed and certified by the manufacturer to be within ±2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternately, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within ±2 percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results. [213]

4. Procedures.

4.1 Pretest Preparations. Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

4.2 Calibration Procedures. Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

Note.—If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

4.3 Individual Source Surveys.

4.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

a. Valves—The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exists the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur. [213]

b. Flanges and Other Connections—For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

c. Pumps and Compressors—Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the

shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

d. Pressure Relief Devices—The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

e. Process Drains—For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

f. Open-Ended Lines or Valves—Place the probe inlet at approximately the center of the opening to the atmosphere.

g. Seal System Degassing Vents and Accumulator Vents—Place the probe inlet at approximately the center of the opening to the atmosphere.

h. Access Door Seals—Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

4.3.2 Type II—"No Detectable Emission". Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration described in 4.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) Pump or Compressor Seals—If applicable, determine the type of shaft seal. Preform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices—If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in this paragraph shall be used to determine if detectable emissions exist.

4.3.3 Alternative Screening Procedure. A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument techniques of 4.3.1 or 4.3.2.

Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or a squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of 4.3.1 or 4.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable. 213

4.4 Instrument Evaluation Procedures. At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 Response Factor. Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 80 percent of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 90 percent of the saturation concentration, or 70 percent of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 5.

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and mutiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

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NSPS REGULATIONS

Subpart VV—Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry [206]

§ 60.480 Applicability and designation of affected facility.

(a)(1) The provisions of this subpart apply to affected facilities in the synthetic organic chemicals manufacturing industry.

(2) The group of all equipment (defined in § 60.481) within a process unit is an affected facility.

(b) Any affected facility under paragraph (a) of this section that commences construction or modification after January 5, 1981, shall be subject to the requirements of this subpart.

(c) Addition or replacement of equipment for the purpose of process improvement which is accomplished without a capital expenditure shall not by itself be considered a modification under this subpart.

(d)(1) If an owner or operator applies for one or more of the exemptions in this paragraph, then the owner or operator shall maintain records as required in § 60.486(j).[227]

(2) Any affected facility that has the design capacity to produce less than 1,000 Mg/yr is exempt from § 60.482.

(3) If an affected facility produces heavy liquid chemicals only from heavy liquid feed or raw materials, then it is exempt from § 60.482.

(4) Any affected facility that produces beverage alcohol is exempt from § 60.482.

(5) Any affected facility that has no equipment in VOC service is exempt from § 60.482.

§ 60.481 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act or in Subpart A of Part 60, and the following terms shall have the specific meanings given them.

"Capital expenditure" means, in addition to the definition in 40 CFR 60.2, an expenditure for a physical or operational change to an existing facility that:

(a) Exceeds P, the product of the facility's replacement cost, R, and an adjusted annual asset guideline repair allowance, A, as reflected by the following equation: $P = R \times A$, where

(1) The adjusted annual asset guideline repair allowance, A, is the product of the percent of the replacement cost, Y, and the applicable basic annual asset guideline repair allowance, B, as reflected by the following equation: $A = Y \times (B \div 100)$.

(2) The percent Y is determined from the following equation: $Y = 1.0 - 0.575 \log X$, where X is [illegible] minus the year of construction; and" [230]

(3) The applicable basic annual asset guideline repair allowance, B, is selected from the following table consistent with the applicable subpart: [227]

TABLE FOR DETERMINING APPLICABLE FOR B

Subpart applicable to facility	Value of B to be used in equation
VV	12.5
DDD	12.5
GGG	7.0
KKK	4.5

"Closed vent system" means a system that is not open to the atmosphere and that is composed of piping, connections, and, if necessary, flow inducing devices that transport gas or vapor from a piece or pieces of equipment to a control device.

"Connector" means flanged, screwed, welded, or other joined fittings used to connect two pipe lines or a pipe line and a piece of process equipment.

"Control device" means an enclosed combustion device, vapor recovery system, or flare.

"Distance piece" means an open or enclosed casing through which the piston rod travels, separating the compressor cylinder from the crankcase.

"Double block and bleed system" means two block valves connected in series with a bleed valve or line that can vent the line between the two block valves. [227]

"Equipment" means each pump, compressor, pressure relief device, sampling connection system, open-ended valve or line, valve, and flange or other connector in VOC service and any devices or systems required by this subpart.

"First attempt at repair" means to take rapid action for the purpose of stopping or reducing leakage of organic material to atmosphere using best practices.

"In gas/vapor service" means that the piece of equipment contains process fluid that is in the gaseous state at operating conditions.

"In heavy liquid service" means that the piece of equipment is not in gas/vapor service or in light liquid service.

"In light liquid service" means that the piece of equipment contains a liquid that meets the conditions specified in § 60.485(e).

"Liquids dripping" means any visible leakage from the seal including spraying, misting, clouding, and ice formation.

"Open-ended valve or line" means any valve, except safety relief valves, having one side of the valve seat in contact with process fluid and one side open to the atmosphere, either directly or through open piping.

"Pressure release" means the emission of materials resulting from system pressure being greater than set pressure of the pressure relief device.

"Process improvement" means routine changes made for safety and occupational health requirements, for energy savings, for better utility, for ease of maintenance and operation, for correction of design deficiencies, for bottleneck removal, for changing product requirements, or for environmental control.

"Process unit" means components assembled to produce, as intermediate or final products, one or more of the chemicals listed in § 60.489 of this part. A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the product.

"Process unit shutdown" means a work practice or operational procedure that stops production from a process unit or part of a process unit. An unscheduled work practice or operational procedure that stops production from a process unit or part of a process unit for less than 24 hours is not a process unit shutdown. The use of spare equipment and technically feasible bypassing of equipment without stopping production are not process unit shutdowns.

"Quarter" means a 3-month period; the first quarter concludes on the last day of the last full month during the 180 days following initial startup.

"Replacement cost" means the capital needed to purchase all the depreciable components in a facility. [227]

"Repaired" means that equipment is adjusted, or otherwise altered, in order to eliminate a leak as indicated by one of the following: an instrument reading or 10,000 ppm or greater, indication of liquids dripping, or indication by a sensor that a seal or barrier fluid system has failed.

"Sensor means a device that measures a physical quantity or the change in a physical quantity such as temperature, pressure, flow rate, pH, or liquid level.

"In-situ sampling systems" means nonextractive samplers or in-line samplers.

"Synthetic organic chemicals manufacturing industry" means the industry that produces, as intermediates or final products, one or more of the chemicals listed in § 60.489.

"In vacuum service" means that equipment is operating at an internal

pressure which is at least 5 kilopascals (kPa) below ambient pressure.

"Volatile organic compounds" or VOC means, for the purposes of this subpart, any reactive organic compounds as defined in § 60.2 Definitions.

"In VOC Service" means that the piece of equipment contains or contacts a process fluid that is at least 10 percent VOC by weight. (The provisions of § 60.485(d) specify how to determine that a piece of equipment is not in VOC service.)

§ 60.482-1 Standards: General.

(a) Each owner or operator subject to the provisions of this subpart shall demonstrate compliance with the requirements of § 60.482-1 to § 60.482-10 for all equipment within 180 days of initial startup.

(b) Compliance with § 60.482-1 to § 60.482-10 will be determined by review of records and reports, review of performance test results, and inspection using the methods and procedures specified in § 60.485.

(c)(1) An owner or operator may request a determination of equivalence of a means of emission limitation to the requirements of § 60.482-2, -3, -5, -6, -7, -8, and -10 as provided in § 60.484.

(2) If the Administrator makes a determination that a means of emission limitation is at least equivalent to the requirements of § 60.482-2, -3, -5, -6, -7, -8, or -10, an owner or operator shall comply with the requirements of that determination.

(d) Equipment that is in vacuum service is excluded from the requirements of § 60.482-2 to § 60.482-10 if it is identified as required in § 60.486(e)(5). [227]

§ 60.482-2 Standards0 Pumps in light liquid service.

(a)(1) Each pump in light liquid service shall be monitored monthly to detect leaks by the methods specified in §60.485(b), except as provided in § 60.482-1(c) and paragraphs (d), (e), and (f) of this section.

(2) Each pump in light liquid service shall be checked by visual inspection each calendar week for indications of liquids dripping from the pump seal.

(b)(1) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(2) If there are indications of liquids dripping from the pump seal, a leak is detected.

(c)(1) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 60.482-9.

(2) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(d) Each pump equipped with a dual mechanical seal system that includes a barrier fluid system is exempt from the requirements of paragraph (a), provided the following requirements are met:

(1) Each dual mechanical seal system is:

(i) Operated with the barrier fluid at a pressure that is at all times greater than the pump stuffing box pressure; or

(ii) Equipment with a barrier fluid degassing reservoir that is connected by a closed vent system to a control device that complies with the requirements of § 60.482-10; or

(iii) Equipped with a system that purges the barrier fluid into a process stream with zero VOC emissions to the atmosphere.

(2) The barrier fluid system is in heavy liquid service or is not in VOC service.

(3) Each barrier fluid system is ›uipped with a sensor that will detect ·ure of the seal system, the barrier ·uid system, or both.

(4) Each pump is checked by visual inspection, each calendar week, for indications of liquids dripping from the pump seals.

(5)(i) Each sensor as described in paragraph (d)(3) is checked daily or is equipped with an audible alarm, and

(ii) The owner or operator determines, based on design considerations and operating experience, a criterion that indicates failure of the seal system, the barrier fluid system, or both.

(6)(i) If there are indications of liquids dripping from the pump seal or the sensor indicates failure of the seal system, the barrier fluid system, or both based on the criterion determined in paragraph (d)(5)(ii), a leak is detected.

(ii) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 60.482-9.

(iii) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(e) Any pump that is designated, as described in § 60.486(e) (1) and (2), for no detectable emission, as indicated by an instrument reading of less than 500 ppm above background, is exempt from the requirements of paragraphs (a), (c), and (d) if the pump:

(1) Has no externally actuated shaft penetrating the pump housing.

(2) Is demonstrated to be operating with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background as measured by the methods specified in § 60.485(c), and

(3) Is tested for compliance with paragraph (e)(2) initially upon designation, annually, and at other times requested by the Administrator.

(f) If any pump is equipped with a closed vent system capable of capturing and transporting any leakage from the seal or seals to a control device that complies with the requirements of § 60.482-10, it is exempt from the paragraphs (a)-(e).

§ 60.482-3 Compressors.

(a) Each compressor shall be equipped with a seal system that includes a barrier fluid system and that prevents leakage of VOC to the atmosphere, except as provided in § 60.482-1(c) and paragraph (h) and (i) of this section.

(b) Each compressor seal system as required in paragraph (a) shall be:

(1) Operated with the barrier fluid at a pressure that is greater than the compressor stuffing box pressure; or

(2) Equipped with a barrier fluid system that is connected by a closed vent system to a control device that complies with the requirements of § 60.482-10; or

(3) Equipped with a system that purges the barrier fluid into a process stream with zero VOC emissions to the atmosphere.

(c) The barrier fluid system shall be in heavy liquid service or shall not be in VOC service.

(d) Each barrier fluid system as described in paragraph (a) shall be equipped with a sensor that will detect failure of the seal system, barrier fluid system, or both.

(e)(1) Each sensor as required in paragraph (d) shall be checked daily or shall be equipped with an audible alarm.

(2) The owner or operator shall determine, based on design considerations and operating experience, a criterion that indicates failure of the seal system, the barrier fluid system, or both.

(f) If the sensor indicates failure of the seal system, the barrier system, or both based on the criterion determined under paragraph (e)(2), a leak is detected.

(g)(1) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 60.482-9.

(2) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(h) A compressor is exempt from the requirements of paragraphs (a) and (b), if it is equipped with a closed vent system capable of capturing and transporting any leakage from the seal

to a control device that complies with the requirements of § 60.482–10, except as provided in § 60.482–3(i).

(i) Any compressor that is designated, as described in § 60.486(e) (1) and (2), for no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, is exempt from the requirements of paragraphs (a)–(h) if the compressor:

(1) Is demonstrated to be operating with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as measured by the methods specified in § 60.485(c); and

(2) Is tested for compliance with paragraph (i)(1) initially upon designation, annually, and at other times requested by the Administrator.

(j) Any existing reciprocating compressor in a process unit which becomes an affected facility under provisions of § 60.14 or 60.15 is exempt from § 60.482 (a), (b), (c), (d), (e), and (h), provided the owner or operator demonstrates that recasting the distance piece or replacing the compressor are the only options available to bring the compressor into compliance with the provisions of § 60.4823 (a), (b), (c), (d), (e), and (h).

§ 60.482–4 Standards: Pressure relief devices in gas/vapor service.

(a) Except during pressure releases, each pressure relief device in gas/vapor service shall be operated with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as determined by the methods specified in § 60.485(c).

(b)(1) After each pressure release, the pressure relief device shall be returned to a condition of no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as soon as practicable, but no later than 5 calendar days after the pressure release, except as provided in § 60.482–9.

(2) No later than 5 calendar days after the pressure release, the pressure relief device shall be monitored to confirm the conditions of no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, by the methods specified in § 60.485(c).

(c) Any pressure relief device that is equipped with a closed vent system capable of capturing and transporting leakage through the pressure relief device to a control device as described in § 60.482–10 is exempted from the requirements of paragraphs (a) and (b).

§ 60.482–5 Standards: Sampling connection systems.

(a) Each sampling connection system shall be equipped with a closed purge system or closed vent system, except as provided in § 60.482–1(c).

(b) Each closed purge system or closed vent system as required in paragraph (a) shall:

(1) Return the purged process fluid directly to the process line with zero VOC emissions to the atmosphere; or

(2) Collect and recycle the purged process fluid with zero VOC emissions to the atmosphere; or

(3) Be designed and operated to capture and transport all the purged process fluid to a control device that complies with the requirements of § 60.482–10.

(c) In-situ sampling systems are exempt from paragraphs (a) and (b).

§ 60.482–6 Standards: Open-ended valves or lines.

(a)(1) Each open-ended valve or line shall be equipped with a cap, blind flange, plug, or a second valve, except as provided in § 60.482–1(c).

(2) The cap, blind flange, plug, or second valve shall seal the open end at all times except during operations requiring process fluid flow through the open-ended valve or line.

(b) Each open-ended valve or line equipped with a second valve shall be operated in a manner such that the valve on the process fluid end is closed before the second valve is closed.

(c) When a double block-and-bleed system is being used, the bleed valve or line may remain open during operations that require venting the line between the block valves but shall comply with paragraph (a) at all other times.[227]

§ 60.482–7 Standards: Valves in gas/vapor service in light liquid service.

(a) Each valve shall be monitored monthly to detect leaks by the methods specified in § 60.485(b) and shall comply with paragraphs (b)–(e), except as provided in paragraphs (f), (g), and (h), § 60.483–1, 2, and § 60.482–1(c).

(b) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(c)(1) Any valve for which a leak is not detected for 2 successive months may be monitored the first month of every quarter, beginning with the next quarter, until a leak is detected.

(2) If a leak is detected, the valve shall be monitored monthly until a leak is not detected for 2 successive months.[227]

(d)(1) When a leak is detected, it shall be repaired as soon as practicable, but no later than 15 calendar days after the leak is detected, except as provided in § 60.482–9.

(2) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(e) First attempts at repair include, but are not limited to, the following best practices where practicable:

(1) Tightening of bonnet bolts;

(2) Replacement of bonnet bolts;

(3) Tightening of packing gland nuts;

(4) Injection of lubricant into lubricated packing.

(f) Any valve that is designated, as described in § 60.486(e)(2), for no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, is exempt from the requirements of paragraph (a) if the valve:

(1) Has no external actuating mechanism in contact with the process fluid,

(2) Is operated with emissions less than 500 ppm above background as determined by the method specified in § 60.485(c), and

(3) Is tested for compliance with paragraph (f)(2) initially upon designation, annually, and at other times requested by the Administrator.

(g) Any valve that is designated, as described in § 60.486(f)(1), as an unsafe-to-monitor valve is exempt from the requirements of paragraph (a) if:

(1) The owner or operator of the valve demonstrates that the valve is unsafe to monitor because monitoring personnel would be exposed to an immediate danger as a consequence of complying with paragraph (a), and

(2) The owner or operator of the valve adheres to a written plan that requires monitoring of the valve as frequently as practicable during safe-to-monitor times.

(h) Any valve that is designated, as described in § 60.486(f)(2), as a difficult-to-monitor valve is exempt from the requirements of paragraph (a) if:

(1) The owner or operator of the valve demonstrates that the valve cannot be monitored without elevating the monitoring personnel more than 2 meters above a support surface.

(2) The process unit within which the valve is located either becomes an affected facility through § 60.14 or § 60.15 or the owner or operator designates less than 3.0 percent of the total number of valves as difficult-to-monitor, and[227]

(3) The owner or operator of the valve follows a written plan that requires monitoring of the valve at least once per calendar year.

§ 60.482–6 Standards: Pumps and valves in heavy liquid service, pressure relief devices in light liquid or heavy liquid service, and flanges and other connectors.

(a) Pumps and valves in heavy liquid service, pressure relief devices in light liquid or heavy liquid service, and flanges and other connectors shall be monitored within 5 days by the method specified in § 60.485(b) if evidence of a potential leak is found by visual, audible, olfactory, or any other detection method.

(b) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(c)(1) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 60.482–9.

(2) The first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(d) First attempts at repair include, but are not limited to, the best practices described under § 60.482–7(e).

§ 60.482–9 Standards: Delay of repair.

(a) Delay of repair of equipment for which leaks have been detected will be allowed if the repair is technically infeasible without a process unit shutdown. Repair of this equipment shall occur before the end of the next process unit shutdown.

(b) Delay of repair of equipment will be allowed for equipment which is isolated from the process and which does not remain in VOC service.

(c) Delay of repair for valves will be allowed if:

(1) The owner or operator demonstrates that emissions of purged material resulting from immediate repair are greater than the fugitive emissions likely to result from delay of repair, and

(2) When repair procedures are effected, the purged material is collected and destroyed or recovered in a control device complying with § 60.482–10.

(d) Delay of repair for pumps will be allowed if:

(1) Repair requires the use of a dual mechanical seal system that includes a barrier fluid system, and

(2) Repair is completed as soon as practicable, but not later than 6 months after the leak was detected.

(e) Delay of repair beyond a process unit shutdown will be allowed for a valve, if valve assembly replacement is necessary during the process unit shutdown, valve assembly supplies have been depleted, and valve assembly supplies had been sufficiently stocked before the supplies were depleted. Delay of repair beyond the next process unit shutdown will not be allowed unless the next process unit shutdown occurs sooner than 6 months after the first process unit shutdown.

§ 60.482–10 Standards: Closed vent systems and control devices.

(a) Owners or operators of closed vent systems and control devices used to comply with provisions of this subpart shall comply with the provisions of this section.

(b) Vapor recovery systems (for example, condensers and adsorbers) shall be designed and operated to recover the VOC emissions vented to them with an efficiency of 95 percent or greater.

(c) Enclosed combustion devices shall be designed and operated to reduce the VOC emissions vented to them with an efficiency of 95 percent or greater, or to provide a minimum residence time of 0.75 seconds at a minimum temperature of 816°C.

(d)(1) Flares shall be designed for and operated with no visible emissions as determined by the methods specified in § 60.485(g), except for periods not to exceed a total of 5 minutes during any 2 consecutive hours.

(2) Flares shall be operated with a flame present at all times, as determined by the methods specified in § 60.485(g).

(3) Flares shall be used only with the net heating value of the gas being combusted being 11.2 MJ/scm (300 Btu/scf) or greater if the flare is steam-assisted or air-assisted; or with the net heating value of the gas being combusted being 7.45 MJ/scm or greater if the flare is nonassisted. The net heating value of the gas being combusted shall be determined by the methods specified in § 60.485(g).

(4) Steam-assisted and nonassisted flares shall be designed for and operated with an exit velocity, as determined by the methods specified in § 60.485(g)(4), less than 18 m/sec (60 ft/sec).

(5) Flares used to comply with this subpart shall be steam-assisted, air-assisted, or nonassisted.

(6) Air-assisted flares shall be designed and operated with an exit velocity less than the velocity, V_{max}, as determined by the methods specified in § 60.485(g)(5).

(e) Owners or operators of control devices used to comply with the provisions of this subpart shall monitor these control devices to ensure that they are operated and maintained in conformance with their designs.

(f)(1) Closed vent systems shall be designed and operated with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background and visual inspections, as determined by the methods specified in § 60.485(c).

(2) Closed vent systems shall be monitored to determine compliance with this section initially in accordance with § 60.8, annually and at other times requested by the Administrator.

(g) Closed vent systems and control devices used to comply with provisions of this subpart shall be operated at all times when emissions may be vented to them.

§ 60.483–1 Alternative standards for valves—allowable percentage of valves leaking.

(a) An owner or operator may elect to comply with an allowable percentage of valves leaking of equal to or less than 2.0 percent.

(b) The following requirements shall be met if an owner or operator wishes to comply with an allowable percentage of valves leaking:

(1) An owner or operator must notify the Administrator that the owner or operator has elected to comply with the allowable percentage of valves leaking before implementing this alternative standard, as specified in § 60.487(b).

(2) A performance test as specified in paragraph (c) of this section shall be conducted initially upon designation, annually, and at other times requested by the Administrator.

(3) If a valve leak is detected, it shall be repaired in accordance with § 60.482–7(d) and (e).

(c) Performance tests shall be conducted in the following manner:

(1) All valves in gas/vapor and light liquid service within the affected facility shall be monitored within 1 week by the methods specified in § 60.485(b).

(2) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(3) The leak percentage shall be determined by dividing the number of valves for which leaks are detected by the number of valves in gas/vapor and light liquid service within the affected facility.

(d) Owners and operators who elect to comply with this alternative standard shall not have an affected facility with a leak percentage greater than 2.0 percent.

§ 60.483–2 Alternative standards for valves—skip period leak detection and repair.

(a)(1) An owner or operator may elect to comply with one of the alternative work practices specified in paragraphs (b) (2) and (3) of this section.

(2) An owner or operator must notify the Administrator before implementing

one of the alternative work practices, as specified in § 60.487(b).

(b)(1) An owner or operator shall comply initially with the requirements for valves in gas/vapor service and valves in light liquid service, as described in § 60.482–7.

(2) After 2 consecutive quarterly leak detection periods with the percent of valves leaking equal to or less than 2.0, an owner or operator may begin to skip 1 of the quarterly leak detection periods for the valves in gas/vapor and light liquid service.

(3) After 5 consecutive quarterly leak detection periods with the percent of valves leaking equal to or less than 2.0, an owner or operator may begin to skip 3 of the quarterly leak detection periods for the valves in gas/vapor and light liquid service.

(4) If the percent of valves leaking is greater than 2.0, the owner or operator shall comply with the requirements as described in § 60.482–7 but can again elect to use this section.

(5) The percent of valves leaking shall be determined by dividing the sum of valves found leaking during current monitoring and valves for which repair has been delayed by the total number of valves subject to the requirements of § 60.483–2.

(6) An owner or operator must keep a record of the percent of valves found leaking during each leak detection period.

§ 60.484 Equivalence of means of emission limitation.

(a) Each owner or operator subject to the provisions of this subpart may apply to the Administrator for determination of equivalance for any means of emission limitation that achieves a reduction in emissions of VOC at least equivalent to the reduction in emissions of VOC achieved by the controls required in this subpart.

(b) Determination of equivalence to the equipment, design, and operational requirements of this subpart will be evaluated by the following guidelines:

(1) Each owner or operator applying for an equivalence determination shall be responsible for collecting and verifying test data to demonstrate equivalence of means of emission limitation.

(2) The Administrator will compare test data for the means of emission limitation to test data for the equipment, design, and operational requirements.

(3) The Administrator may condition the approval of equivalence on requirements that may be necessary to assure operation and maintenance to achieve the same emission reduction as the equipment, design, and operational requirements.

(c) Determination of equivalence to the required work practices in this subpart will be evaluated by the following guidelines:

(1) Each owner or operator applying for a determination of equivalence shall be responsible for collecting and verifying test data to demonstrate equivalence of an equivalent means of emission limitation.

(2) For each affected facility for which a determination of equivalence is requested, the emission reduction achieved by the required work practice shall be demonstrated.

(3) For each affected facility, for which a determination of equivalence is requested, the emission reduction achieved by the equivalent means of emission limitation shall be demonstrated.

(4) Each owner or operator applying for a determination of equivalence shall commit in writing to work practice(s) that provide for emission reductions equal to or greater than the emission reductions achieved by the required work practice.

(5) The Administrator will compare the demonstrated emission reduction for the equivalent means of emission limitation to the demonstrated emission reduction for the required work practices and will consider the commitment in paragraph (c)(4).

(6) The Administrator may condition the approval of equivalence on requirements that may be necessary to assure operation and maintenance to achieve the same emission reduction as the required work practice.

(d) An owner or operator may offer a unique approach to demonstrate the equivalence of any equivalent means of emission limitation.

(e)(1) After a request for determination of equivalence is received, the Administrator will publish a notice in the Federal Register and provide the opportunity for public hearing if the Administrator judges that the request may be approved.

(2) After notice and opportunity for public hearing, the Administrator will determine the equivalence of a means of emission limitation and will publish the determination in the Federal Register.

(3) Any equivalent means of emission limitations approved under this section shall constitute a required work practice, equipment, design, or operational standard within the meaning of Section 111(h)(1) of the Clean Air Act.

(f)(1) Manufacturers of equipment used to control equipment leaks of VOC may apply to the Administrator for determination of equivalence for any equivalent means of emission limitation that achieves a reduction in emissions of VOC achieved by the equipment, design, and operational requirements of this subpart.

(2) The Administrator will make an equivalence determination according to the provisions of paragraphs (b), (c), (d), and (e).

§ 60.485 Test methods and procedures.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the test method and procedure requirements provided in this section.

(b) Monitoring, as required in §§ 60.482, 60.483, and 60.484, shall comply with the following requirements:

(1) Monitoring shall comply with Reference Method 21.

(2) The detection instrument shall meet the performance criteria of Reference Method 21.

(3) The instrument shall be calibrated before use on each day of its use by the methods specified in Method 21.

(4) Calibration gases shall be:

(i) Zero air (less than 10 ppm of hydrocarbon in air); and

(ii) A mixture of methane or n-hexane and air at a concentration of approximately, but less than, 10,000 ppm methane or n-hexane.

(5) The instrument probe shall be traversed around all potential leak interfaces as close to the interface as possible as described in Reference Method 21.

(c) When equipment is tested for compliance with no detectable emissions as required in § 60.482–2(e), –3(i), –4, –7(f), and –10(e), the test shall comply with the following requirements:

(1) The requirements of paragraphs (b)(1)–(4) shall apply.

(2) The background level shall be determined, as set forth in Reference Method 21.

(3) The instrument probe shall be traversed around all potential leak interfaces as close to the interface as possible as described in Reference Method 21.

(4) The arithmetic difference between the maximum concentration indicated by the instrument and the background level is compared with 500 ppm for determining compliance.

(d)(1) Each piece of equipment within a process unit is presumed to be in VOC service unless an owner or operator demonstrates that the piece of equipment is not in VOC service. For a piece of equipment to be considered not in VOC service, it must be determined that the percent VOC content can be reasonably expected never to exceed 10 percent by weight. For purposes of

determining the percent VOC content in the process fluid that is contained in or contacts equipment, procedures that conform to the general methods described in ASTM E–260, E–168, E–169 (incorporated by reference as specified in § 60.17) shall be used.

(2) If an owner or operator decides to exclude non-reactive organic compounds from the total quantity of organic compounds in determining the percent VOC content of the process fluid, the exclusion will be allowed if:

(i) Those substances excluded are those considered as having negligible photochemical reactivity by the Administrator; and

(ii) The owner or operator demonstrates that the percent organic content, excluding non-reactive organic compounds, can be reasonably expected never to exceed 10 percent by weight.

(3)(i) An owner or operator may use engineering judgment rather than the procedures in paragraphs (d) (1) and (2) of this section to demonstrate that the percent VOC content does not exceed 10 percent by weight, provided that the engineering judgment demonstrates that the VOC content clearly does not exceed 10 percent by weight. When an owner or operator and the Administrator do not agree on whether a piece of equipment is not in VOC service, however, the procedures in paragraphs (d) (1) and (2) shall be used to resolve the disagreement.

(ii) If an owner or operator determines that a piece of equipment is in VOC service, the determination can be revised only after following the procedures in paragraphs (d) (1) and (2).

(e) Equipment is in light liquid service if the following conditions apply:

(1) The vapor pressure of one or more of the components is greater than 0.3 kPa at 20° C. Vapor pressures may be obtained from standard reference texts or may be determined by ASTM D–2879 (incorporated by reference as specified in § 60.17).

(2) The total concentration of the pure components having a vapor pressure greater than 0.3 kPa at 20° C is equal to or greater than 20 percent by weight; and

(3) The fluid is a liquid at operating conditions.

(f) Samples used in conjunction with paragraphs (d), (e), and (g) shall be representative of the process fluid that is contained in or contacts the equipment or the gas being combusted in the flare.

(g)(1) Reference Method 22 shall be used to determine the compliance of flares with the visible emission provisions of this subpart.

(2) The presence of a flare pilot flame shall be monitored using a thermocouple or any other equivalent device to detect the presence of a flame.

(3) The net heating value of the gas being combusted in a flare shall be calculated using the following equation:

$$H_T = K\left(\sum_{i=1}^{n} C_i H_i\right)$$

Where:

H_T = Net heating value of the sample, MJ/scm; where the net enthalpy per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°.

$$K = \text{Constant, } 1.740 \times 10^{-7}\left(\frac{1}{\text{ppm}}\right)\left(\frac{\text{g mole}}{\text{scm}}\right)\left(\frac{\text{MJ}}{\text{kcal}}\right)$$

where

$$\text{standard temperature for } \frac{\text{g mole}}{\text{scm}} \text{ is } 20°\text{C}$$

C_i = Concentration of sample component i in ppm, as measured by Reference Method 18 and ASTM D2504–67 (reapproved 1977) (incorporated by reference as specified in § 60.17).

H_i = Net heat of combustion of sample component i, kcal/g mole. The heats of combustion may be determined using ASTM D2382–76 (incorporated by reference as specified in § 60.17) if published values are not available or cannot be calculated.

(4) The actual exit velocity of a flare shall be determined by dividing the volumetric flowrate (in units of standard temperature and pressure), as determined by Reference Method 2, 2A, 2C, or 2D as appropriate; by the unobstructed (free) cross sectional area of the flare tip.

(5) The maximum permitted velocity, V_{max}, for air-assisted flares shall be determined by the following equation:

$$V_{max} = 8.706 + 0.7084(H_T)$$

V_{max} = Maximum permitted velocity, m/sec.

8.706 = Constant.

0.7084 = Constant.

H_T = The net heating value as determined in paragraph (g)(4).

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414))

§ 60.486 Recordkeeping requirements.

(a)(1) Each owner or operator subject to the provisions of this subpart shall comply with the recordkeeping requirements of this section.

(2) An owner or operator of more than one affected facility subject to the provisions of this subpart may comply with the recordkeeping requirements for these facilities in one recordkeeping system if the system identifies each record by each facility.

(b) When each leak is detected as specified in § 60.482–2, -3, -7, -8, and § 60.483–2, the following requirements apply:

(1) A weatherproof and readily visible identification, marked with the equipment identification number, shall be attached to the leaking equipment.

(2) The identification on a valve may be removed after it has been monitored for 2 successive months as specified in § 60.482–7(c) and no leak has been detected during those 2 months.

(3) The identification on equipment except on a valve, may be removed after it has been repaired.

(c) When each leak is detected as specified in § 60.482–2, -3, -7, -8, and § 60.483–2, the following information shall be recorded in a log and shall be kept for 2 years in a readily accessible location:

(1) The instrument and operator identification numbers and the equipment identification number.

(2) The date the leak was detected and the dates of each attempt to repair the leak.

(3) Repair methods applied in each attempt to repair the leak.

(4) "Above 10,000" if the maximum instrument reading measured by the methods specified in § 60.485(a) after each repair attempt is equal to or greater than 10,000 ppm.

(5) "Repair delayed" and the reason for the delay if a leak is not repaired within 15 calendar days after discovery of the leak.

(6) The signature of the owner or operator (or designate) whose decision it was that repair could not be effected without a process shutdown.

(7) The expected date of successful repair of the leak if a leak is not repaired within 15 days.

(8) Dates of process unit shutdown that occur while the equipment is unrepaired.

(9) The date of successful repair of the leak.

(d) The following information pertaining to the design requirements for closed vent systems and control devices described in § 60.482–10 shall be recorded and kept in a readily accessible location:

(1) Detailed schematics, design specifications, and piping and instrumentation diagrams.

(2) The dates and descriptions of any changes in the design specifications.

(3) A description of the parameter or parameters monitored, as required in § 60.482–10(e), to ensure that control devices are operated and maintained in

conformance with their design and an explanation of why that parameter (or parameters) was selected for the monitoring.

(4) Periods when the closed vent systems and control devices required in § 60.482–2, -3, -4, and -5 are not operated as designed, including periods when a flare pilot light does not have a flame.

(5) Dates of startups and shutdowns of the closed vent systems and control devices required in § 60.482–2, -3, -4, and -5.

(e) The following information pertaining to all equipment subject to the requirements in § 60.482–1 to -10 shall be recorded in a log that is kept in a readily accessible location:

(1) A list of identification numbers for equipment subject to the requirements of this subpart.

(2)(i) A list of identification numbers for equipment that are designated for no detectable emissions under the provisions of § 60.482–2(e), -3(i) and -7(f).

(ii) The designation of equipment as subject to the requirements of § 60.482–2(e), -3(i), or -7(f) shall be signed by the owner or operator.

(3) A list of equipment identification numbers for pressure relief devices required to comply with § 60.482–4.

(4)(i) The dates of each compliance test as required in § 60.482–2(e), -3(i), -4, and -7(f).

(ii) The background level measured during each compliance test.

(iii) The maximum instrument reading measured at the equipment during each compliance test.

(5) A list of identification numbers for equipment in vacum service.

(f) The following information pertaining to all valves subject to the requirements of § 60.482–7 (g) and (h) shall be recorded in a log that is kept in a readily accessible location:

(1) A list of identification numbers for valves that are designated as unsafe-to-monitor, an explanation for each valve stating why the valve is unsafe-to-monitor, and the plan for monitoring each valve.

(2) A list of identification numbers for valves that are designated as difficult-to-monitor, an explanation for each valve stating why the valve is difficult-to-monitor, and the schedule for monitoring each value.

(g) The following information shall be recorded for valves complying with § 60.483–2:

(1) A schedule of monitoring

(2) The percent of valves found leaking during each monitoring period.

(h) The following information shall be recorded in a log that is kept in a readily accessible location:

(1) Design criterion required in § 60.482–2(d)(5) and § 60.482–3(e)(2) and explanation of the design criterion; and

(2) Any changes to this criterion and the reasons for the changes.

(i) The following information shall be recorded in a log that is kept in a readily accessible location for use in determining exemptions as provided in § 60.480(d):

(1) An analysis demonstrating the design capacity of the affected facility.

(2) A statement listing the feed or raw materials and products from the affected facilities and an analysis demonstrating whether these chemicals are heavy liquids or beverage alcohol, and

(3) An analysis demonstrating that equipment is not in VOC service.

(j) Information and data used to demonstrate that a piece of equipment is not in VOC service shall be recorded in a log that is kept in a readily accessible location.

(k) The provisions of §§ 60.7 (b) and (d) do not apply to affected facilities subject to this subpart.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414))

(Approved by the Office of Management and Budget under the control number 2060–0012)

§ 60.487 Reporting Requirements.

(a) Each owner or operator subject to the provisions of this subpart shall submit semiannual reports to the Administrator beginning six months after the initial start up date.

(b) The initial semiannual report to the Administrator shall include the following information:

(1) Process unit identification.

(2) Number of valves subject to the requirements of § 60.482–7, excluding those valves designated for no detectable emissions under the provisions of § 60.482–7(f).

(3) Number of pumps subject to the requirements of § 60.482–2, excluding those pumps designated for no detectable emissions under the provisions of § 60.482–2(e) and those pumps complying with § 60.482–2(f).

(4) Number of compressors subject to the requirements of § 60.482–3, excluding those compressors designated for no detectable emissions under the provisions of § 60.482–3(i) and those compressors complying with § 60.482–3(h).

(c) All semiannual reports to the Administrator shall include the following information, summarized from the information in § 60.486:

(1) Process unit identification.

(2) For each month during the semiannual reporting period,

(i) Number of valves for which leaks were detected as described in § 60.482(7)(b) or § 60.483–2,

(ii) Number of valves for which leaks were not reported as repaired in § 60.482–7(d)(1),[227]

(iii) Number of pumps for which leaks were detected as described in §§ 60.482–2(b) and (d)(6)(i),

(iv) Number of pumps for which leaks erer not repaired as required in §§ 60.482–2(c)(1) and (d)(6)(ii),

(v) Number of compressors for which leaks were detected as desctibed in § 60.482–3(f),

(vi) Number of compressors for which leaks were not repaired as required in § 60.482–3(g)(1), and[227]

(vii) The facts that explain each delay of repair and, where appropriate, why a process unit shutdown was technically infeasible.

(3) Dates of process unit shutdowns which occurred within the semiannual reporting period.

(4) Revisions to items reported according to paragraph (b) if changes have occurred since the initial report or subsequent revisions to the initial report.

(d) An owner or opertor electing to comply with the provisions of §§ 60.483–1 and –2 shall notify the Administrator of the alternative standard selected 90 days before implementing either of the provisions.

(e) An owner or operator shall report the results of all performance tests in accordance with § 60.8 of the General Provisions. The provisions of § 60.8(d) do not apply to affected facilities subject to the provisions of this subpart except that an owner or operator must notify the Administrator of the schedule for the initial performance tests at least 30 days before the initial performance tests.

(f) The requirements of paragraphs (a) through (c) of this subsection remain in force until and unless EPA, in delegating enforcement authority to a State under Section 111(c) of the Act, approves reporting requirements or an alternative means of compliance surveillance adopted by such State. In that event, affected sources within the State will be relieved of the obligation to comply with the requirements of paragraphs (a) through (c) of this subsection, provided that they comply with the requirements established by the State.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414))

Approved by the Office of Management and Budget under the control number 2060–0012)

§ 60.488 Reconstruction.

For the purposes of this subpart:

(a) The cost of the following frequently replaced components of the facility shall not be considered in calculating either the "fixed capital cost of the new components" or the "fixed capital costs that would be required to construct a comparable new facility" under § 60.15: pump seals, nuts and bolts, rupture disks, and packings.

(b) Under § 60.15, the "fixed capital cost of new components" includes the fixed capital cost of all depreciable components (except components specified in § 60.488 (a)) which are or will be replaced pursuant to all continuous programs of component replacement which are commenced within any 2-year period following the applicability date for the appropriate subpart. (See the "Applicability and designation of affected facility" section of the appropriate subpart.) For purposes of this paragraph, "commenced" means that an owner or operator has undertaken a continuous program of component replacement or that an owner or operator has entered into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of component replacement.

§ 60.489 List of chemicals produced by affected facilities.

(a) The following chemicals are produced, as intermediates or final products, by process units covered under this subpart. The applicability date for process units producing one or more of these chemicals is January 5, 1981.

CAS No. *	Chemical
105-57-7	Acetal.
75-07-0	Acetaldehyde.
107-89-1	Acetaldol.
60-35-5	Acetamide.
103-84-4	Acetanilide.
64-19-7	Acetic acid.
108-24-7	Acetic anhydride.
67-64-1	Acetone.
75-86-5	Acetone cyanohydrin.
75-05-8	Acetonitrile.
98-86-2	Acetophenone.
75-36-5	Acetyl chloride.
74-86-2	Acetylene.
107-02-8	Acrolein.
79-06-1	Acrylamide.
79-10-7	Acrylic acid.
107-13-1	Acrylonitrile.
124-04-9	Adipic acid.
111-69-3	Adiponitrile.
(**)	Alkyl naphthalenes.
107-18-6	Allyl alcohol.
107-05-1	Allyl chloride.
1321-11-5	Aminobenzoic acid.
111-41-1	Aminoethylethanolamine.
123-30-8	p-Aminophenol.
628-63-7, 123-92-2	Amyl acetates.
71-41-0 *	Amyl alcohols.
110-58-7	Amyl amine.
543-59-9	Amyl chloride.
110-66-7 *	Amyl mercaptans.
1322-06-1	Amyl phenol.

CAS No. *	Chemical
62-53-3	Aniline.
142-04-1	Aniline hydrochloride.
29191-52-4	Anisidine.
100-66-3	Anisole.
118-92-3	Anthranilic acid.
84-65-1	Anthraquinone.
100-52-7	Benzaldehyde.
55-21-0	Benzamide.
71-43-2	Benzene.
98-48-6	Benzenedisulfonic acid.
98-11-3	Benzenesulfonic acid.
134-81-6	Benzil.
76-93-7	Benzilic acid.
65-85-0	Benzoic acid.
119-53-9	Benzoin.
100-47-0	Benzonitrile.
119-61-9	Benzophenone.
98-07-7	Benzotrichloride.
98-88-4	Benzoyl chloride.
100-51-6	Benzyl alcohol.
100-46-9	Benzylamine.
120-51-4	Benzyl benzoate.
100-44-7	Benzyl chloride.
98-87-3	Benzyl dichloride.
92-52-4	Biphenyl.
80-05-7	Bisphenol A.
10-86-1	Bromobenzene.
27497-51-4	Bromonaphthalene.
106-99-0	Butadiene.
106-98-9	1-butene.
123-86-4	n-butyl acetate.
141-32-2	n-butyl acrylate.
71-36-3	n-butyl alcohol.
78-92-2	s-butyl alcohol.
75-65-0	t-butyl alcohol.
109-73-9	n-butylamine.
13952-84-6	s-butylamine.
75-64-9	t-butylamine.
98-73-7	p-tert-butyl benzoic acid.
107-88-0	1,3-butylene glycol.
123-72-8	n-butyraldehyde.
107-92-6	Butyric acid.
106-31-0	Butyric anhydride.
109-74-0	Butyronitrile.
105-60-2	Caprolactam.
75-1-50	Carbon disulfide.
558-13-4	Carbon tetrabromide.
56-23-5	Carbon tetrachloride.
9004-35-7	Cellulose acetate.
79-11-8	Chloroacetic acid
108-42-9	m-chloroaniline.
95-51-2	o-chloroaniline.
106-47-8	p-chloroaniline.
35913-09-8	Chlorobenzaldehyde.
108-90-7	Chlorobenzene
118-91-2, 535-80-8, 74-11-3 *	Chlorobenzoic acid.
2136-81-4, 2136-89-2, 5216-25-1*	Chlorobenzotrichloride.
1371-03-5	Chlorobenzoyl chloride.
25497-29-4	Chlorodifluoromethane.
75-45-6	Chlorodifluoroethane.
67-66-3	Chloroform.
25586-43-0	Chloronaphthalene.
88-73-3	o-chloronitrobenzene.
100-00-5	p-chloronitrobenzene.
25167-80-0	Chlorophenols.
126-99-8	Chloroprene.
7790-94-5	Chlorosulfonic acid.
108-41-8	m-chlorotoluene.
95-49-8	o-chlorotoluene.
106-43-4	p-chlorotoluene.
75-72-9	Chlorotrifluoromethane.
108-39-4	m-cresol.
95-48-7	o-cresol.
106-44-5	p-cresol.
1319-77-3	Mixed cresols.
1319-77-3	Cresylic acid.
4170-30-0	Crotonaldehyde
3724-65-0	Crotonic acid.
98-82-8	Cumene.
80-15-9	Cumene hydroperoxide.
372-09-8	Cyanoacetic acid.
506-77-4	Cyanogen chloride.
108-80-5	Cyanuric acid.
108-77-0	Cyanuric chloride.
110-82-7	Cyclohexane.
108-93-0	Cyclohexanol.
108-94-1	Cyclohexanone.
110-83-8	Cyclohexene.
108-91-8	Cyclohexylamine.
111-78-4	Cyclooctadiene.
112-30-1	Decanol.

CAS No. *	Chemical
123-42-2	Diacetone alcohol
27576-04-1	Diaminobenzoic acid.
95-76-1, 95-82-9, 554-00-7, 608-27-5, 608-31-1, 695-43-7, 27134-27-6, 57311-92-9 *	Dichloroaniline
541-73-1	m-dichlorobenzene
95-50-1	o-dichlorobenzene
106-46-7	p-dichlorobenzene.
75-71-8	Dichlorodifluoromethane
111-44-4	Dichloroethyl ether
107-06-2	1,2-dichloroethane (EDC).
96-23-1	Dichlorohydrin.
26952-23-8	Dichloropropene.
101-83-7	Dicyclohexylamine
109-89-7	Diethylamine.
111-46-6	Diethylene glycol.
112-36-7	Diethylene glycol diethyl ether
111-96-6	Diethylene glycol dimethyl ether
112-34-5	Diethylene glycol monobutyl ether.
124-17-7	Diethylene glycol monobutyl ether acetate.
111-90-0	Diethylene glycol monoethyl ether.
112-15-2	Diethylene glycol monoethyl ether acetate.
111-77-3	Diethylene glycol monomethyl ether
64-67-5	Diethyl sulfate.
75-37-6	Difluoroethane.
25167-70-8	Diisobutylene.
26761-40-0	Diisodecyl phthalate.
27554-26-3	Diisooctyl phthalate.
674-82-8	Diketene.
124-40-3	Dimethylamine.
121-69-7	N,N-dimethylaniline.
115-10-6	N,N-dimethyl ether.
68-12-2	N,N-dimethylformamide
57-14-7	Dimethylhydrazine
77-78-1	Dimethyl sulfate.
75-18-3	Dimethyl sulfide.
67-68-5	Dimethyl sulfoxide
120-61-6	Dimethyl terephthalate
99-34-3	3,5-dinitrobenzoic acid
51-28-5	Dinitrophenol.
25321-14-6	Dinitrotoluene.
123-91-1	Dioxane.
646-06-0	Dioxolane
122-39-4	Diphenylamine.
101-84-8	Diphenyl oxide.
102-08-9	Diphenyl thiourea.
25265-71-8	Dipropylene glycol.
25378-22-7	Dodecene.
26675-17-4	Dodecylaniline.
27193-86-8	Dodecylphenol
106-89-8	Epichlorohydrin.
64-17-5	Ethanol.
141-43-5 *	Ethanolamines.
141-78-6	Ethyl acetate.
141-97-9	Ethyl acetoacetate.
140-88-5	Ethyl acrylate.
75-04-7	Ethylamine
100-41-4	Ethylbenzene.
74-96-4	Ethyl bromide.
9004-57-3	Ethylcellulose.
75-00-3	Ethyl chloride
105-39-5	Ethyl chloroacetate.
105-56-6	Ethylcyanoacetate.
74-85-1	Ethylene.
96-49-1	Ethylene carbonate.
107-07-3	Ethylene chlorohydrin.
107-15-3	Ethylenediamine.
106-93-4	Ethylene dibromide.
107-21-1	Ethylene glycol.
111-55-7	Ethylene glycol diacetate.
110-71-4	Ethylene glycol dimethyl ether
111-76-2	Ethylene glycol monobutyl ether.
112-07-2	Ethylene glycol monobutyl ether acetate.
110-80-5	Ethylene glycol monoethyl ether.
111-15-9	Ethylene glycol monoethyl ether acetate.
109-86-4	Ethylene glycol monomethyl ether.
110-49-6	Ethylene glycol monomethyl ether acetate
122-99-6	Ethylene glycol monophenyl ether.
2807-30-9	Ethylene glycol monopropyl ether
75-21-8	Ethylene oxide.
60-29-7	Ethyl ether
104-76-7	2-ethylhexanol.
122-51-0	Ethyl orthoformate
96-92-1	Ethyl oxalate.
41892-71-1	Ethyl sodium oxalacetate
50-00-0	Formaldehyde
75-12-7	Formamide.

CAS No. *	Chemical
64-18-6	Formic acid.
110-17-8	Fumaric acid.
98-01-1	Furfural.
56-81-5	Glycerol.
26545-73-7	Glycerol dichlorohydrin.
25791-96-2	Glycerol triether.
56-40-6	Glycine.
107-22-2	Glyoxal.
118-74-1	Hexachlorobenzene.
67-72-1	Hexachloroethane.
36653-82-4	Hexadecyl alcohol.
124-09-4	Hexamethylenediamine.
629-11-8	Hexamethylene glycol.
100-97-0	Hexamethylenetetramine.
74-90-8	Hydrogen cyanide.
123-31-9	Hydroquinone.
99-96-7	p-hydroxybenzoic acid.
26760-64-5	Isoamylene.
78-83-1	Isobutanol.
110-19-0	Isobutyl acetate.
115-11-7	Isobutylene.
78-84-2	Isobutyraldehyde.
79-31-2	Isobutyric acid.
25339-17-7	Isodecanol.
26952-21-6	Isooctyl alcohol.
78-78-4	Isopentane.
78-59-1	Isophorone.
121-91-5	Isophthalic acid.
78-79-5	Isoprene.
67-63-0	Isopropanol.
108-21-4	Isopropyl acetate.
75-31-0	Isopropylamine.
75-29-6	Isopropyl chloride.
25168-06-3	Isopropylphenol.
463-51-4	Ketene.
(*)	Linear alkyl sulfonate.
123-01-3	Linear alkylbenzene (linear dodecylbenzene).
110-16-7	Maleic acid.
108-31-6	Maleic anhydride.
6915-15-7	Malic acid.
141-78-7	Mesityl oxide.
121-47-1	Metanilic acid.
79-41-4	Methacrylic acid.
563-47-3	Methallyl chloride.
67-56-1	Methanol.
79-20-9	Methyl acetate.
105-45-3	Methyl acetoacetate.
74-89-5	Methylamine.
100-61-8	n-methylaniline.
74-83-9	Methyl bromide.
37385-71-2	Methyl butynol.
74-87-3	Methyl chloride.
108-87-2	Methylcyclohexane.
1331-22-2	Methylcyclohexanone.
75-09-2	Methylene chloride.
101-77-9	Methylene dianiline.
101-68-8	Methylene diphenyl diisocyanate.
78-93-3	Methyl ethyl ketone.
107-31-3	Methyl formate.
108-11-2	Methyl isobutyl carbinol.
108-10-1	Methyl isobutyl ketone.
80-62-6	Methyl methacrylate.
77-75-8	Methylpentynol.
98-83-9	a-methylstyrene.
110-91-8	Morpholine.
85-47-2	a-naphthalene sulfonic acid.
120-18-3	b-naphthalene sulfonic acid.
90-15-3	a-naphthol.
135-19-3	b-naphthol.
76-98-9	Neopentanoic acid.
88-74-4	o-nitroaniline.
100-01-6	p-nitroaniline.
91-23-6	o-nitroanisole.
100-17-4	p-nitroanisole.
98-95-3	Nitrobenzene.
27178-83-2*	Nitrobenzoic acid (o,m, and p).
79-24-3	Nitroethane.
75-52-5	Nitromethane.
88-75-5	2-Nitrophenol.
25322-01-4	Nitropropane.
1321-12-6	Nitrotoluene.
27215-95-8	Nonene.
25154-52-3	Nonylphenol.
27193-28-8	Octylphenol.
123-63-7	Paraldehyde.
115-77-5	Pentaerythritol.
109-66-0	n-pentane.
109-67-1	1-pentene.
127-18-4	Perchloroethylene.
594-42-3	Perchloromethyl mercaptan.
94-70-2	o-phenetidine.
156-43-4	p-phenetidine.
108-95-2	Phenol.

CAS No. *	Chemical
98-67-9, 585-38-6, 609-46-1, 1333-39-7*	Phenolsulfonic acids.
91-40-7	Phenyl anthranilic acid.
(*)	Phenylenediamine.
75-44-5	Phosgene.
85-44-9	Phthalic anhydride.
85-41-6	Phthalimide.
108-99-6	b-picoline.
110-85-0	Piperazine.
9003-29-6, 25038-59-7*	Polybutenes.
25322-68-3	Polyethylene glycol.
25322-69-4	Polypropylene glycol.
123-38-6	Propional dehyde.
79-09-4	Propionic acid.
71-23-8	n-propyl alcohol.
107-10-8	Propylamine.
540-54-5	Propyl chloride.
115-07-1	Propylene.
127-00-4	Propylene chlorohydrin.
78-87-5	Propylene dichloride.
57-55-6	Propylene glycol.
75-56-9	Propylene oxide.
110-86-1	Pyridine.
106-51-4	Quinone.
108-46-3	Resorcinol.
27138-57-4	Resorcylic acid.
69-72-7	Salicylic acid.
127-09-3	Sodium acetate.
532-32-1	Sodium benzoate.
9004-32-4	Sodium carboxymethyl cellulose.
3926-62-3	Sodium chloroacetate.
141-53-7	Sodium formate.
139-02-6	Sodium phenate.
110-44-1	Sorbic acid.
100-42-5	Styrene.
110-15-6	Succinic acid.
110-61-2	Succinonitrile.
121-57-3	Sulfanilic acid.
126-33-0	Sulfolane.
1401-55-4	Tannic acid.
100-21-0	Terephthalic acid.
79-34-5*	Tetrachloroethanes.
117-08-8	Tetrachlorophthalic anhydride.
78-00-2	Tetraethyl lead.
119-64-2	Tetrahydronaphthalene.
85-43-8	Tetrahydrophthalic anhydride.
75-74-1	Tetramethyl lead.
110-60-1	Tetramethylenediamine.
110-18-9	Tetramethylethylenediamine.
108-88-3	Toluene.
95-80-7	Toluene-2,4-diamine.
584-84-9	Toluene-2,4-diisocyanate.
26471-62-5	Toluene diisocyanates (mixture).
1333-07-9	Toluenesulfonamide.
104-15-4*	Toluenesulfonic acids.
98-59-9	Toluenesulfonyl chloride.
26915-12-8	Toluidines.
87-61-6, 108-70-3, 120-82-1*	Trichlorobenzenes.
71-55-6	1,1,1-trichloroethane.
79-00-5	1,1,2-trichloroethane.
79-01-6	Trichloroethylene.
75-69-4	Trichlorofluoromethane.
96-18-4	1,2,3-trichloropropane.
76-13-1	1,1,2-trichloro-1,2,2-trifluoroethane.
121-44-8	Triethylamine.
112-27-6	Triethylene glycol.
112-49-2	Triethylene glycol dimethyl ether.
7756-94-7	Triisobutylene.
75-50-3	Trimethylamine.
57-13-6	Urea.
108-05-4	Vinyl acetate.
75-01-4	Vinyl chloride.
75-35-4	Vinylidene chloride.
25013-15-4	Vinyl toluene.
1330-20-7	Xylenes (mixed).
95-47-6	o-xylene.
106-42-3	p-xylene.
1300-71-6	Xylenol.
1300-73-8	Xylidine.

* CAS numbers refer to the Chemical Abstracts Registry numbers assigned to specific chemicals, isomers, or mixtures of chemicals. Some isomers or mixtures that are covered by the standards do not have CAS numbers assigned to them. The standards apply to all of the chemicals listed, whether CAS numbers have been assigned or not.

* No CAS number(s) have been assigned to this chemical, its isomers, or mixtures containing these chemicals.

* CAS numbers for some of the isomers are listed; the standards apply to all of the isomers and mixtures, even if CAS numbers have not been assigned.

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Subpart XX—Standards of Performance for Bulk Gasoline Terminals [195]

§ 60.500 Applicability and designation of affected facility.

(a) The affected facility to which the provisions of this subpart apply is the total of all the loading racks at a bulk gasoline terminal which deliver liquid product into gasoline tank trucks.

(b) Each facility under paragraph (a) of this section, the construction or modification of which is commenced after December 17, 1980, is subject to the provisions of this subpart.

(c) For purposes of this subpart, any replacement of components of an existing facility, described in paragraph § 60.500(a), commenced before August 18, 1983 in order to comply with any emission standard adopted by a State or political subdivision thereof will not be considered a reconstruction under the provisions of 40 CFR 60.15.

[Note: The intent of these standards is to minimize the emissions of VOC through the application of best demonstrated technologies (BDT). The numerical emission limits in this standard are expressed in terms of total organic compounds. This emission limit reflects the performance of BDT.]

§ 60.501 Definitions.

The terms used in this subpart are defined in the Clean Air Act, in § 60.2 of this part, or in this section as follows:

"Bulk gasoline terminal" means any gasoline facility which receives gasoline by pipeline, ship or barge, and has a gasoline throughput greater than 75,700 liters per day. Gasoline throughput shall be the maximum calculated design throughput as may be limited by compliance with an enforceable condition under Federal, State or local law and discoverable by the Administrator and any other person.

"Continuous vapor processing system" means a vapor processing system that treats total organic compounds vapors collected from gasoline tank trucks on a demand basis without intermediate accumulation in a vapor holder.

"Existing vapor processing system" means a vapor processing system [capable of achieving emissions to the atmosphere no greater than 80 milligrams of total organic compounds per liter of gasoline loaded], the construction or refurbishment of which was commenced before December 17, 1980, and which was not constructed or refurbished after that date.

"Gasoline" means any petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

"Gasoline tank truck" means a delivery tank truck used at bulk gasoline terminals which is loading gasoline or which has loaded gasoline on the immediately previous load.

"Intermittent vapor processing system" means a vapor processing system that employs an intermediate vapor holder to accumulate total organic compounds vapors collected from gasoline tank trucks, and treats the accumulated vapors only during automatically controlled cycles.

"Loading rack" means the loading arms, pumps, meters, shutoff valves, relief valves, and other piping and valves necessary to fill delivery tank trucks.

"Refurbishment" means, with reference to a vapor processing system, replacement of components of, or addition of components to, the system within any 2-year period such that the fixed capital cost of the new components required for such component replacement or addition exceeds 50 percent of the cost of a comparable entirely new system.

"Total organic compounds" means those compounds measured according to the procedures in § 60.503.

"Vapor collection system" means any equipment used for containing total organic compounds vapors displaced during the loading of gasoline tank trucks.

"Vapor processing system" means all equipment used for recovering or oxidizing total organic compounds vapors displaced from the affected facility.

"Vapor-tight gasoline tank truck" means a gasoline tank truck which has demonstrated within the 12 preceding months that its product delivery tank will sustain a pressure change of not more than 750 pascals (75 mm of water) within 5 minutes after it is pressurized to 4,500 pascals (450 mm of water). This capability is to be demonstrated using the pressure test procedure specified in Reference Method 27.

§ 60.502 Standard for Volatile Organic Compound (VOC) emissions from bulk gasoline terminals.

On and after the date on which § 60.8(a) requires a performance test to be completed, the owner or operator of each bulk gasoline terminal containing an affected facility shall comply with the requirements of this section. [213]

(a) Each affected facility shall be equipped with a vapor collection system designed to collect the total organic compounds vapors displaced from tank trucks during product loading.

(b) The emissions to the atmosphere from the vapor collection system due to the loading of liquid product into gasoline tank trucks are not to exceed 35 milligrams of total organic compounds per liter of gasoline loaded, except as noted in paragraph (c) of this section.

(c) For each affected facility equipped with an existing vapor processing system, the emissions to the atmosphere from the vapor collection system due to the loading of liquid product into gasoline tank trucks are not to exceed 80 milligrams of total organic compounds per liter of gasoline loaded.

(d) Each vapor collection system shall be designed to prevent any total organic compounds vapors collected at one loading rack from passing to another loading rack.

(e) Loadings of liquid product into gasoline tank trucks shall be limited to vapor-tight gasoline tank trucks using the following procedures:

(1) The owner or operator shall obtain the vapor tightness documentation described in § 60.505(b) for each gasoline tank truck which is to be loaded at the affected facility.

(2) The owner or operator shall require the tank identification number to be recorded as each gasoline tank truck is loaded at the affected facility.

(3) The owner or operator shall cross-check each tank identification number obtained in (e)(2) of this section with the file of tank vapor tightness documentation within 2 weeks after the corresponding tank is loaded.

(4) The terminal owner or operator shall notify the owner or operator of each nonvapor-tight gasoline tank truck loaded at the affected facility within 3 weeks after the loading has occurred.

(5) The terminal owner or operator shall take steps assuring that the nonvapor-tight gasoline tank truck will not be reloaded at the affected facility until vapor tightness documentation for that tank is obtained.

(6) Alternate procedures to those described in (e)(1) through (5) of this section for limiting gasoline tank truck loadings may be used upon application to, and approval by, the Administrator.

(f) The owner or operator shall act to assure that loadings of gasoline tank trucks at the affected facility are made only into tanks equipped with vapor collection equipment that is compatible with the terminal's vapor collection system.

(g) The owner or operator shall act to assure that the terminal's and the tank truck's vapor collection systems are connected during each loading of a gasoline tank truck at the affected facility. Examples of actions to

accomplish this include training drivers in the hookup procedures and posting visible reminder signs at the affected loading racks.

(h) The vapor collection and liquid loading equipment shall be designed and operated to prevent gauge pressure in the delivery tank from exceeding 4.500 pascals (450 mm of water) during product loading. This level is not to be exceeded when measured by the procedures specified in § 60.503(b).

(i) No pressure-vacuum vent in the bulk gasoline terminal's vapor collection system shall begin to open at a system pressure less than 4.500 pascals (450 mm of water).

(j) Each calendar month, the vapor collection system, the vapor processing system, and each loading rack handling gasoline shall be inspected during the loading of gasoline tank trucks for total organic compounds liquid or vapor leaks. For purposes of this paragraph, detection methods incorporating sight, sound, or smell are acceptable. Each detection of a leak shall be recorded and the source of the leak repaired within 15 calendar days after it is detected.

(Approved by the Office of Management and Budget under control number 2060-0006)

§ 60.503 Test methods and procedures.

(a) Section 60.8(f) does not apply to the performance test procedures required by this subpart.

(b) For the purpose of determining compliance with § 60.502(h), the following procedures shall be used:

(1) Calibrate and install a pressure measurement device (liquid manometer, magnehelic gauge, or equivalent instrument), capable of measuring up to 500 mm of water gauge pressure with ±2.5 mm of water precision.

(2) Connect the pressure measurement device to a pressure tap in the terminal's vapor collection system, located as close as possible to the connection with the gasoline tank truck.

(3) During the performance test, record the pressure every 5 minutes while a gasoline tank truck is being loaded, and record the highest instantaneous pressure that occurs during each loading. Every loading position must be tested at least once during the performance test. 213

(c) For the purpose of determining compliance with the mass emission limitations of § 60.502(b) and (c), the following reference methods shall be used:

(1) For the determination of volume at the exhaust vent:

(i) Method 2B for combustion vapor processing systems.

(ii) Method 2A for all other vapor processing systems.

(2) For the determination of total organic compounds concentration at the exhaust vent, Method 25A or 25B. The calibration gas shall be either propane or butane.

(d) Immediately prior to a performance test required for determination of compliance with § 60.502(b), (c), and (h), all potential sources of vapor leakage in the terminal's vapor collection system equipment shall be monitored for leaks using Method 21. The monitoring shall be conducted only while a gasoline tank truck is being loaded. A reading of 10,000 ppmv or greater as methane shall be considered a leak. All leaks shall be repaired prior to conducting the performance test.

(e) The test procedure for determining compliance with § 60.502(b) and (c) is as follows:

(1) All testing equipment shall be prepared and installed as specified in the appropriate test methods.

(2) The time period for a performance test shall be not less than 6 hours, during which at least 300,000 liters of gasoline are loaded. If the throughput criterion is not met during the initial 6 hours, the test may be either continued until the throughput criterion is met, or resumed the next day with another complete 6 hours of testing. As much as possible, testing should be conducted during the 6-hour period in which the highest throughput normally occurs.

(3) For intermittent vapor processing systems:

(i) The vapor holder level shall be recorded at the start of the performance test. The end of the performance test shall coincide with a time when the vapor holder is at its original level.

(ii) At least two startups and shutdowns of the vapor processor shall occur during the performance test. If this does not occur under automatically controlled operation, the system shall be manually controlled.

(4) The volume of gasoline dispensed during the performance test period at all loading racks whose vapor emissions are controlled by the processing system being tested shall be determined. This volume may be determined from terminal records or from gasoline dispensing meters at each loading rack.

(5) An emission testing interval shall consist of each 5-minute period during the performance test. For each interval:

(i) The reading from each measurement instrument shall be recorded, and

(ii) The volume exhausted and the average total organic compounds concentration in the exhaust vent shall be determined, as specified in the appropriate test method. The average total organic compounds concentration shall correspond to the volume measurement by taking into account the sampling system response time.

(6) The mass emitted during each testing interval shall be calculated as follows:

$$M_{oi} = 10^{-6} K V_{si} C_{ti}$$

where:

M_{oi} = mass of total organic compounds emitted during testing interval i, mg

V_{si} = volume of air-vapor mixture exhausted, m^3, at standard conditions.

C_{ti} = total organic compounds concentration (as measured) at the exhaust vent, ppmv

K = density of calibration gas, mg/m^3, at standard conditions

$= 1.83 \times 10^6$, for propane

$= 2.41 \times 10^6$, for butane 213

s = standard conditions, 20°C and 760 mm Hg.

(7) The total organic compounds mass emissions shall be calculated as follows:

$$E = \frac{\sum_{i=1}^{n} M_{oi}}{L}$$

where: 213

E = mass of total organic compounds emitted per volume of gasoline loaded, mg/liter.

M_{oi} = mass of total organic compounds emitted during testing interval i, mg.

L = total volume of gasoline loaded, liters.

n = number of testing intervals.

(f) The owner or operator may adjust the emission results to exclude the methane and ethane content in the exhaust vent by any method approved by the Administrator.

[Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)]

(Approved by the Office of Management and Budget under control number 2060-0006.)

§ 60.504 [Reserved]

§ 60.505 Reporting and recordkeeping.

(a) The tank truck vapor tightness documentation required under 160.502(e)(1) shall be kept on file at the terminal in a permanent form available for inspection.

(b) The documentation file for each gasoline tank truck shall be updated at least once per year to reflect current test results as determined by Method 27. This documentation shall include, as a minimum, the following information:

(1) Test Title: Gasoline Delivery Tank Pressure Test—EPA Reference Method 27.

(2) Tank Owner and Address.
(3) Tank Identification Number.
(4) Testing Location.
(5) Date of Test.
(6) Tester Name and Signature.
(7) Witnessing Inspector, if any: Name, Signature, and Affiliation.
(8) Test Results: Actual Pressure Change in 5 minutes, mm of water (average for 2 runs).

(c) A record of each monthly leak inspection required under § 60.502(j) shall be kept on file at the terminal for at least 2 years. Inspection records shall include, as a minimum, the following information:
(1) Date of Inspection.
(2) Findings (may indicate no leaks discovered; or location, nature, and severity of each leak).
(3) Leak determination method.
(4) Corrective Action (date each leak repaired; reasons for any repair interval in excess of 15 days).
(5) Inspector Name and Signature.

(d) The terminal owner or operator shall keep documentation of all notifications required under § 60.502(e)(4) on file at the terminal for at least 2 years.

(e) [Reserved].

(f) The owner or operator of an affected facility shall keep records of all replacements or additions of components performed on an existing vapor processing system for at least 3 years.

[Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)]

[Approved by the Office of Management and Budget under control number 2060-0006.]

§ 60.506 Reconstruction.

For purposes of this subpart:

(a) The cost of the following frequently replaced components of the affected facility shall not be considered in calculating either the "fixed capital cost of the new components" or the "fixed capital costs that would be required to construct a comparable entirely new facility" under § 60.15: pump seals, loading arm gaskets and swivels, coupler gaskets, overfill sensor couplers and cables, flexible vapor hoses, and grounding cables and connectors.

(b) Under § 60.15, the "fixed capital cost of the new components" includes the fixed capital cost of all depreciable components [except components specified in § 60.506(a)] which are or will be replaced pursuant to all continuous programs of component replacement which are commenced within any 2-year period following December 17, 1980. For purposes of this paragraph, "commenced" means that an owner or operator has undertaken a continuous program of component replacement or that an owner or operator has entered into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of component replacement.

[Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)]

Proposed/effective
45 FR 83126, 12/17/80

Promulgated
48 FR 37578, 8/18/83 (195)

Revised
48 FR 56580, 12/22/83 (213)

Subpart GGG—Standards of Performance for Equipment Leaks of VOC in Petroleum Refineries [227]

§ 60.590 Applicability and designation of affected facility.

(a)(1) The provisions of this subpart apply to affected facilities in petroleum refineries.

(2) A compressor is an affected facility.

(3) The group of all the equipment (defined in § 60.591) within a process unit is an affected facility.

(b) Any affected facility under paragraph (a) of this section that commences construction or modification after January 4, 1983, is subject to the requirements of this subpart.

(c) Addition or replacement of equipment (defined in § 60.591) for the purpose of process improvement which is accomplished without a capital expenditure shall not by itself be considered a modification under this subpart.

(d) Facilities subject to Subpart VV or Subpart KKK of 40 CFR Part 60 are excluded from this subpart.

§ 60.591 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act, in Subpart A of Part 60, or in Subpart VV of Part 60, and the following terms shall have the specific meanings given them.

"Alaskan North Slope" means the approximately 69,000 square mile area extending from the Brooks Range to the Arctic Ocean.

"Equipment" means each valve, pump, pressure relief device, sampling connection system, open-ended valve or line, and flange or other connector in VOC service. For the purposes of recordkeeping and reporting only, compressors are considered equipment.

"In Hydrogen Service" means that a compressor contains a process fluid that meets the conditions specified in § 60.593(b).

"In Light Liquid Service" means that the piece of equipment contains a liquid that meets the conditions specified in § 60.593(c).

"Petroleum Refinery" means any facility engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, or other products through the distillation of petroleum, or through the redistillation, cracking, or reforming of unfinished petroleum derivatives.

"Petroleum" means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

"Process Unit" means components assembled to produce intermediate or final products from petroleum, unfinished petroleum derivatives, or other intermediates; a process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the product.

§ 60.592 Standards.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the requirements of § 60.482-1 to § 60.482-10 as soon as practicable, but no later than 180 days after initial startup.

(b) An owner or operator may elect to comply with the requirements of § 60.483-1 and § 60.483-2.

(c) An owner or operator may apply to the Administrator for a determination of equivalency for any means of emission limitation that achieves a reduction in emissions of VOC at least equivalent to the reduction in emissions of VOC achieved by the controls required in this subpart. In doing so, the owner or operator shall comply with requirements of § 60.484.

(d) Each owner or operator subject to the provisions of this subpart shall comply with the provisions of § 60.485 except as provided in § 60.593.

(e) Each owner or operator subject to the provisions of this subpart shall comply with the provisions of § 60.486 and § 60.487.

(Sec. 114 of Clean Air Act as amended (42 U.S.C. 7414))

§ 60.593 Exceptions.

(a) Each owner or operator subject to the provisions of this subpart may comply with the following exceptions to the provisions of Subpart VV.

(b)(1) Compressors in hydrogen service are exempt from the requirements of § 60.592 if an owner or operator demonstrates that a compressor is in hydrogen service.

(2) Each compressor is presumed not be be in hydrogen service unless an owner or operator demonstrates that the piece of equipment is in hydrogen service. For a piece of equipment to be considered in hydrogen service, it must be determined that the percent hydrogen content can be reasonably expected always to exceed 50 percent by volume. For purposes of determining the percent hydrogen content in the process fluid that is contained in or contacts a compressor, procedures that conform to the general method described in ASTM E-260, E-168, or E-169 (incorporated by reference as specified in §60.17) shall be used.

(3)(i) An owner or operator may use engineering judgment rather than procedures in paragraph (b)(2) of this section to demonstrate that the percent content exceeds 50 percent by volume, provided the engineering judgment demonstrates that the content clearly exceeds 50 percent by volume. When an owner or operator and the Administrator do not agree on whether a piece of equipment is in hydrogen service, however, the procedures in paragraph (b)(2) shall be used to resolve the disagreement.

(ii) If an owner or operator determines that a piece of equipment is in hydrogen service, the determination can be revised only after following the procedures in paragraph (b)(2).

(c) Any existing reciprocating compressor that becomes an affected facility under provisions of § 60.14 or § 60.15 is exempt from § 60.482 (a), (b), (c), (d), (e), and (h) provided the owner or operator demonstrates that recasting the distance piece or replacing the compressor are the only options available to bring the compressor into compliance with the provisions of § 60.482 (a), (b), (c), (d), (e), and (h).

(d) An owner or operator may use the following provision in addition to § 60.485(e): Equipment is in light liquid service if the percent evaporated is greater than 10 percent at 150°C as determined by ASTM Method D-86 (incorporated by reference as specified in § 60.18).

(e) Pumps in light liquid service and valves in gas/vapor and light liquid service within a process unit that is located in the Alaskan North Slope are exempt from the requirements of § 60.482-2 and § 60.482-7.

Proposed/effective

48 FR 279, 1/4/83

Promulgated

49 FR 22598, 5/30/84 (227)

PART 60—[AMENDED]

40 CFR Part 60 is amended as follows:

1. By adding a new Subpart GGG as follows:

Subpart GGG—Standards of Performance for Equipment Leaks of VOC in Petroleum Refineries

Sec.

60.590 Applicability and designation of affected facility.
60.591 Definitions.
60.592 Standards.
60.593 Exceptions.
60.594–60.599 [Reserved]

Subpart GGG—Standards of Performance for Equipment Leaks of VOC in Petroleum Refineries

§ 60.590 Applicability and designation of affected facility.

(a)(1) The provisions of this subpart apply to affected facilities in petroleum refineries.

(2) A compressor is an affected facility.

(3) The group of all the equipment (defined in § 60.591) within a process unit is an affected facility.

(b) Any affected facility under paragraph (a) of this section that commences construction or modification after January 4, 1983, is subject to the requirements of this subpart.

(c) Addition or replacement of equipment (defined in § 60.591) for the purpose of process improvement which is accomplished without a capital expenditure shall not by itself be considered a modification under this subpart.

(d) Facilities subject to Subpart VV or Subpart KKK of 40 CFR Part 60 are excluded from this subpart.

§ 60.591 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act, in Subpart A of Part 60, or in Subpart VV of Part 60, and the following terms shall have the specific meanings given them.

"Alaskan North Slope" means the approximately 69,000 square mile area extending from the Brooks Range to the Arctic Ocean.

"Equipment" means each valve, pump, pressure relief device, sampling connection system, open-ended valve or line, and flange or other connector in VOC service. For the purposes of recordkeeping and reporting only, compressors are considered equipment.

"In Hydrogen Service" means that a compressor contains a process fluid that meets the conditions specified in § 60.593(b).

"In Light Liquid Service" means that the piece of equipment contains a liquid that meets the conditions specified in § 60.593(c).

"Petroleum Refinery" means any facility engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, or other products through the distillation of petroleum, or through the redistillation, cracking, or reforming of unfinished petroleum derivatives.

"Petroleum" means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

"Process Unit" means components assembled to produce intermediate or final products from petroleum, unfinished petroleum derivatives, or other intermediates; a process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the product.

§ 60.592 Standards.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the requirements of § 60.482–1 to § 60.482–10 as soon as practicable, but no later than 180 days after initial startup.

(b) An owner or operator may elect to comply with the requirements of § 60.483–1 and § 60.483–2.

(c) An owner or operator may apply to the Administrator for a determination of equivalency for any means of emission limitation that achieves a reduction in emissions of VOC at least equivalent to the reduction in emissions of VOC achieved by the controls required in this subpart. In doing so, the owner or operator shall comply with requirements of § 60.484.

(d) Each owner or operator subject to the provisions of this subpart shall comply with the provisions of § 60.485 except as provided in § 60.593.

(e) Each owner or operator subject to the provisions of this subpart shall comply with the provisions of § 60.486 and § 60.487.

(Sec. 114 of Clean Air Act as amended (42 U.S.C. 7414))

§ 60.593 Exceptions.

(a) Each owner or operator subject to the provisions of this subpart may comply with the following exceptions to the provisions of Subpart VV.

(b)(1) Compressors in hydrogen service are exempt from the requirements of § 60.592 if an owner or operator demonstrates that a compressor is in hydrogen service.

(2) Each compressor is presumed not be be in hydrogen service unless an owner or operator demonstrates that the piece of equipment is in hydrogen service. For a piece of equipment to be considered in hydrogen service, it must be determined that the percent hydrogen content can be reasonably expected always to exceed 50 percent by volume. For purposes of determining the percent hydrogen content in the process fluid that is contained in or contacts a compressor, procedures that conform to the general method described in ASTM E–260, E–168, or E–169 (incorporated by reference as specified in §60.17) shall be used.

(3)(i) An owner or operator may use engineering judgment rather than procedures in paragraph (b)(2) of this section to demonstrate that the percent content exceeds 50 percent by volume, provided the engineering judgment demonstrates that the content clearly exceeds 50 percent by volume. When an owner or operator and the Administrator do not agree on whether a piece of equipment is in hydrogen service, however, the procedures in paragraph (b)(2) shall be used to resolve the disagreement.

(ii) If an owner or operator determines that a piece of equipment is in hydrogen service, the determination can be revised only after following the procedures in paragraph (b)(2).

(c) Any existing reciprocating compressor that becomes an affected facility under provisions of § 60.14 or § 60.15 is exempt from § 60.482 (a), (b), (c), (d), (e), and (h) provided the owner or operator demonstrates that recasting the distance piece or replacing the compressor are the only options available to bring the compressor into compliance with the provisions of § 60.482 (a), (b), (c), (d), (e), and (h).

(d) An owner or operator may use the following provision in addition to § 60.485(e): Equipment is in light liquid service if the percent evaporated is greater than 10 percent at 150°C as determined by ASTM Method D–86 (incorporated by reference as specified in § 60.18).

(e) Pumps in light liquid service and valves in gas/vapor and light liquid service within a process unit that is located in the Alaskan North Slope are exempt from the requirements of § 60.482–2 and § 60.482–7.

2. By adding in alphabetical order the new terms "capital expenditure," "double block and bleed system," and "replacement cost" in § 60.481 of Subpart VV as follows:

§ 60.481 Definitions.

* * * * *

"Capital expenditure" means, in addition to the definition in 40 CFR 60.2, an expenditure for a physical or operational change to an existing facility that:

(a) Exceeds P, the product of the facility's replacement cost, R, and an adjusted annual asset guideline repair allowance, A, as reflected by the following equation: $P = R \times A$, where

(1) The adjusted annual asset guideline repair allowance, A, is the product of the percent of the replacement cost, Y, and the applicable basic annual asset guideline repair allowance, B, as reflected by the following equation: $A = Y \times (B \div 100)$;

(2) The percent Y is determined from the following equation: $Y = 1.0 - 0.575 \log X$, where X is the year of construction; and

(3) The applicable basic annual asset guideline repair allowance, B, is selected from the following table consistent with the applicable subpart:

TABLE FOR DETERMINING APPLICABLE FOR B

Subpart applicable to facility	Value of B to be used in equation
VV	12.5
DDD	12.5
GGG	7.0
KKK	4.5

* * * * *

"Double block and bleed system" means two block valves connected in series with a bleed valve or line that can vent the line between the two block valves.

* * * * *

"Replacement cost" means the capital needed to purchase all the depreciable components in a facility.

* * * * *

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

3. By adding paragraph (c) to § 60.482–6 as follows:

§ 60.482–6 Standards: Open-ended valves or lines.

* * * * *

(c) When a double block-and-bleed system is being used, the bleed valve or line may remain open during operations that require venting the line between the block valves but shall comply with paragraph (a) at all other times.

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

4. By revising paragraph (d)(1) of § 60.480 as follows:

§ 60.480 Applicability and designation of affected facility.

* * * * *

(d)(1) If an owner or operator applies for one or more of the exemptions in this paragraph, then the owner or operator shall maintain records as required in § 60.486(i).

* * * * *

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

5. By revising paragraph (d) of § 60.482–1 as follows:

§ 60.482-1 Standards: General.

* * * * *

(d) Equipment that is in vacuum service is excluded from the requirements of § 60.482-2 to § 60.482-10 if it is identified as required in § 60.486(e)(5).

(Sections 111, 114, and 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7414, 7601(a)))

6. By revising paragraph (c)(2) and paragraph (h)(2) of § 60.482-7 as follows:

§ 60.482-7 Standards: Valves in gas/vapor and in light liquid service.

* * * * *

(c) * * *

(2) If a leak is detected, the valve shall be monitored monthly until a leak is not detected for 2 successive months.

* * * * *

(h) * * *

(2) The process unit within which the valve is located either becomes an affected facility through § 60.14 or § 60.15 or the owner or operator designates less than 3.0 percent of the total number of valves as difficult-to-monitor, and

* * * * *

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

7. By revising paragraphs (c)(2) (ii) and (vi) of § 60.487 as follows:

§ 60.487 Reporting requirements.

* * * * *

(c) * * *

(2) * * *

(ii) Number of valves for which leaks were not repaired as required in § 60.482-7(d)(1),

* * * * *

(vi) Number of compressors for which leaks were not repaired as required in § 60.482-3(g)(1), and

* * * * *

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

(Approved by the Office of Management and Budget under control number 2060-0067.)

8. By adding § 60.488 to Subpart VV as follows:

§ 60.488 Reconstruction.

For the purposes of this subpart:

(a) The cost of the following frequently replaced components of the facility shall not be considered in calculating either the "fixed capital cost of the new components" or the "fixed capital costs that would be required to construct a comparable new facility" under § 60.15: pump seals, nuts and bolts, rupture disks, and packings.

(b) Under § 60.15, the "fixed capital cost of new components" includes the fixed capital cost of all depreciable components (except components specified in § 60.488 (a)) which are or will be replaced pursuant to all continuous programs of component replacement which are commenced within any 2-year period following the applicability date for the appropriate subpart. (See the "Applicability and designation of affected facility" section of the appropriate subpart.) For purposes of this paragraph, "commenced" means that an owner or operator has undertaken a continuous program of component replacement or that an owner or operator has entered into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of component replacement.

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

9. By revising paragraphs (a) (34), (35), and (36) by adding (a)(4) of § 60.17 of Subpart A—General Provisions as follows:

§ 60.17 Incorporation by reference.

(a) * * *

(34) ASTM E169-63 (Reapproved 1977), General Techniques of Ultraviolet Quantitative Analysis, IBR approved for § 60.485(d) and § 60.593(b).

(35) ASTM E168-67 (Reapproved 1977), General Techniques of Infrared Quantitative Analysis, IBR approved for § 60.485(d) and § 60.593(b).

(36) ASTM E260-73, General Gas Chromatography Procedures, IBR approved for § 60.485(d) and § 60.593(b).

* * * * *

(40) ASTM D86-78, Distillation of Petroleum Products, IBR approved for § 60.593(d).

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

Appendix A [Amended]

10. By redesignating the heading "5.2 Apparatus" as "5.1 Apparatus" in Method 18 of Appendix A as follows:

* * * * *

5.1 Apparatus

* * * * *

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

11. By revising the first equation in Section 6.2.1.1 in Method 18 of Appendix A as follows:

$$Q_2 = Q_1 \sqrt{\frac{P_2 T_1}{P_1 T_2}} \quad \text{Eq. 18-1}$$

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

12. By revising the citation "Citation 21 in section 8." to "Citation 18 in section 8." in 6.2.1.1 in Method 18 of Appendix A.

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

13. By changing the word "caped" to "capped" in section 6.2.2.1 in Method 18 of Appendix A.

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

14. By changing all the "mg/liter" to "g/liter" in section 6.2.2.3 in Method 18 of Appendix A.

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

15. By changing the word "with" to "within" in section 7.4.4.3 in Method 18 of Appendix A.

(Sections 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7414, 7601(a)))

[FR Doc. 84-13849 Filed 5-29-84; 8:45 am]

BILLING CODE 6560-50-M

PART 60—[AMENDED]

40 CFR Part 60 is amended as follows:

1. The authority citation for Part 60 continues to read as follows:

Authority: 42 U.S.C. 7411, 7601(a).

2. By adding a new Subpart KKK as follows:

Subpart KKK—Standards of Performance for Equipment Leaks of VOC From Onshore Natural Gas Processing Plants

Sec.

60.630 Applicability and designation of affected facility.
60.631 Definitions.
60.632 Standards.
60.633 Exceptions.
60.634 Alternative means of emission limitation.
60.635 Recordkeeping requirements.
60.636 Reporting requirements.
60.637–60.639 [Reserved].

Subpart KKK—Standards of Performance for Equipment Leaks of VOC From Onshore Natural Gas Processing Plants

§ 60.630 Applicability and designation of affected facility.

(a)(1) The provisions of this subpart apply to affected facilities in onshore natural gas processing plants.

(2) A compressor in VOC service or in wet gas service is an affected facility.

(3) The group of all equipment except compressors (defined in § 60.631) within a process unit is an affected facility.

(b) Any affected facility under paragraph (a) of this section that commences construction, reconstruction, or modification after January 20, 1984, is subject to the requirements of this subpart.

(c) Addition or replacement of equipment (defined in § 60.631) for the purpose of process improvement that is accomplished without a capital expenditure shall not by itself be considered a modification under this subpart.

(d) Facilities covered by Subpart VV or Subpart GGG of 40 CFR Part 60 are excluded from this subpart.

(e) A compressor station, dehydration unit, sweetening unit, underground storage tank, field gas gathering system, or liquefied natural gas unit is covered by this subpart if it is located at an onshore natural gas processing plant. If the unit is not located at the plant site, then it is exempt from the provisions of this subpart.

§ 60.631 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act, in Subpart A of Part 60, or in Subpart VV of Part 60; and the following terms shall have the specific meanings given them.

"Alaskan North Slope" means the approximately 69,000 square-mile area extending from the Brooks Range to the Arctic Ocean.

"Equipment" means each pump, pressure relief device, open-ended valve or line, valve, compressor, and flange or other connector that is in VOC service or in wet gas service, and any device or system required by this subpart.

"Field gas" means feedstock gas entering the natural gas processing plant.

"In light liquid service" means that the piece of equipment contains a liquid that meets the conditions specified in § 60.485(e) or § 60.636(h)(2).

"Natural gas liquids" means the hydrocarbons, such as ethane, propane, butane, and pentane, that are extracted from field gas.

"Natural gas processing plant" (gas plant) means any processing site engaged in the extraction of natural gas liquids from field gas, fractionation of mixed natural gas liquids to natural gas products, or both.

"Nonfractionating plant" means any gas plant that does not fractionate mixed natural gas liquids into natural gas products.

"Onshore" means all facilities except those that are located in the territorial seas or on the outer continental shelf.

"Process unit" means equipment assembled for the extraction of natural gas liquids from field gas, the fractionation of the liquids into natural gas products, or other operations associated with the processing of natural gas products. A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the products.

"Reciprocating compressor" means a piece of equipment that increases the pressure of a process gas by positive displacement, employing linear movement of the driveshaft.

"In wet gas service" means that a piece of equipment contains or contacts the field gas before the extraction step in the process.

§ 60.632 Standards.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the requirements of § 60.482–1 (a), (b), and (d) and § 60.482–2 through § 60.482–10, except as provided in § 60.633, as soon as practicable, but no later than 180 days after initial startup.

(b) An owner or operator may elect to comply with the requirements of § 60.483–1 and § 60.483–2.

(c) An owner or operator may apply to the Administrator for permission to use an alternative means of emission limitation that achieves a reduction in emissions of VOC at least equivalent to that achieved by the controls required in this subpart. In doing so, the owner or operator shall comply with requirements of § 60.634 of this subpart.

(d) Each owner or operator subject to the provisions of this subpart shall comply with the provisions of § 60.485 except as provided in § 60.633(f) of this subpart.

(e) Each owner or operator subject to the provisions of this subpart shall comply with the provisions of § 60.486 and § 60.487 except as provided in § 60.633, § 60.635, and § 60.636 of this subpart.

(f) An owner or operator shall use the following provision instead of § 60.485(d)(1): Each piece of equipment is presumed to be in VOC service or in wet gas service unless an owner or operator demonstrates that the piece of equipment is not in VOC service or in wet gas service. For a piece of equipment to be considered not in VOC service, it must be determined that the percent VOC content can be reasonably expected never to exceed 10.0 percent by weight. For a piece of equipment to be considered in wet gas service, it must be determined that it contains or contacts the field gas before the extraction step in the process. For purposes of determining the percent VOC content of the process fluid that is contained in or contacts a piece of equipment, procedures that conform to the methods described in ASTM Methods E169, E168, or E260 (incorporated by reference as specified in § 60.17) shall be used.

§ 60.633 Exceptions.

(a) Each owner or operator subject to the provisions of this subpart may comply with the following exceptions to the provisions of Subpart VV.

(b) (1) Each pressure relief device in gas/vapor service may be monitored quarterly and within 5 days after each pressure release to detect leaks by the methods specified in § 60.485(b) except as provided in § 60.632(c), paragraph (b)(4) of this section, and § 60.482–4(a)–(c) of Subpart VV.

(2) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(3) (i) When a leak is detected, it shall be repaired as soon as practicable, but no later than 15 calendar days after it is detected, except as provided in § 60.482–9.

(ii) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(4) (i) Any pressure relief device that is located in a nonfractionating plant that is monitored only by nonplant personnel may be monitored after a pressure release the next time the monitoring personnel are on site, instead of within 5 days as specified in paragraph (b)(1) of this section and § 60.482–(b)(1) of Subpart VV.

(ii) No pressure relief device described in paragraph (b)(4)(i) of this section shall be allowed to operate for more than 30 days after a pressure release without monitoring.

(c) Sampling connection systems are exempt from the requirements of § 60.482–5.

(d) Pumps in light liquid service, valves in gas/vapor and light liquid service, and pressure relief devices in gas/vapor service that are located at a nonfractionating plant that does not have the design capacity to process 283,000 standard cubic meters per day (scmd) (10 million standard cubic feet per day (scfd)) or more of field gas are exempt from the routine monitoring requirements of § 60.482–2(a)(1), § 60.482–7(a), and § 60.633(b)(1).

(e) Pumps in light liquid service, valves in gas/vapor and light liquid service, and pressure relief devices in gas/vapor service within a process unit that is located in the Alaskan North Slope are exempt from the routine monitoring requirements of § 60.482–2(a)(1), § 60.482–7(a), and § 60.633(b)(1).

(f) Reciprocating compressors in wet gas service are exempt from the compressor control requirements of § 60.482–3.

(g) In addition to the requirements for flares at § 60.482–10(d)(4), the following are allowed:

(1) Steam-assisted and nonassisted flares designed for and operated with an exit velocity, as determined by the methods specified in § 60.485(g)(4), equal to or greater than 18.3 m/sec (60 ft/sec) but less than 122m/sec (400 ft/sec) if the net heating value of the gas being combusted is greater than 37.3 MJ/scm (1000 Btu/scf).

(2) Steam-assisted and nonassisted flares designed for and operated with an exit velocity, as determined by the methods specified in § 60.485(g)(4), less than 122 m/sec (400 ft/sec) and less than the velocity, ^{v}max, as determined by the following equation:

$\text{Log}_{10}(^{v}max) = (H_T + 28.8)/31.7$

^{v}max = Maximum permitted velocity, m/sec.
28.8 = Constant.
31.7 = Constant.
H_T = The net heating value as determined in § 60.485 (g)(3).

(h) An owner or operator may use the following provisions instead of § 60.485(e):

(1) Equipment is in heavy liquid service if the weight percent evaporated is 10 percent or less at 150 °C as determined by ASTM Method D86 (incorporated by reference as specified in § 60.17).

(2) Equipment is in light liquid service if the weight percent evaporated is greater than 10 percent at 150 °C as determined by ASTM Method D86 (incorporated by reference as specified in § 60.17).

§ 60.634 Alternative means of emission limitation.

(a) If, in the Administrator's judgment, an alternative means of emission limitation will achieve a reduction in VOC emissions at least equivalent to the reduction in VOC emissions achieved under any design, equipment, work practice or operational standard, the Administrator will publish, in the Federal Register a notice permitting the use of that alternative means for the purpose of compliance with that standard. The notice may condition permission on requirements related to the operation and maintenance of the alternative means.

(b) Any notice under paragraph (a) of this section shall be published only after notice and an opportunity for a public hearing.

(c) The Administrator will consider applications under this section from either owners or operators of affected facilities, or manufacturers of control equipment.

(d) The Administrator will treat applications under this section according to the following criteria, except in cases where he concludes that other criteria are appropriate:

(1) The applicant must collect, verify and submit test data, covering a period of at least 12 months, necessary to support the finding in paragraph (a) of this section.

(2) If the applicant is an owner or operator of an affected facility, he must commit in writing to operate and maintain the alternative means so as to achieve a reduction in VOC emissions at least equivalent to the reduction in VOC emissions achieved under the design, equipment, work practice or operational standard.

§ 60.635 Recordkeeping requirements.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the requirements of paragraphs (b) and (c) of this section in addition to the requirements of § 60.486.

(b) The following recordkeeping requirements shall apply to pressure relief devices subject to the requirements of § 60.633(b)(1) of this subpart.

(1) When each leak is detected as specified in § 60.633(b)(2), a weatherproof and readily visible identification, marked with the equipment identification number, shall be attached to the leaking equipment. The identification on the pressure relief device may be removed after it has been repaired.

(2) When each leak is detected as specified in § 60.633(b)(2), the following information shall be recorded in a log and shall be kept for 2 years in a readily accessible location:

(i) The instrument and operator identification numbers and the equipment identification number.

(ii) The date the leak was detected and the dates of each attempt to repair the leak.

(iii) Repair methods applied in each attempt to repair the leak.

(iv) "Above 10,000 ppm" if the maximum instrument reading measured by the methods specified in § 60.635(a) after each repair attempt is 10,000 ppm or greater.

(v) "Repair delayed" and the reason for the delay if a leak is not repaired within 15 calendar days after discovery of the leak.

(vi) The signature of the owner or operator (or designate) whose decision it was that repair could not be effected without a process shutdown.

(vii) The expected date of successful repair of the leak if a leak is not repaired within 15 days.

(viii) Dates of process unit shutdowns that occur while the equipment is unrepaired.

(ix) The date of successful repair of the leak.

(x) A list of identification numbers for equipment that are designated for no detectable emissions under the provisions of § 60.482–4(a). The designation of equipment subject to the provisions of § 60.482–4(a) shall be signed by the owner or operator.

(c) An owner or operator shall comply with the following requirement in addition to the requirement of § 60.486(j): Information and data used to demonstrate that a reciprocating compressor is in wet gas service to apply for the exemption in § 60.633(f) shall be recorded in a log that is kept in a readily accessible location.

(Approved by the Office of Management and Budget under control number 2060–0120)

§ 60.636 Reporting requirements.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the requirements of paragraphs (b) and (c) of this section in addition to the requirements of § 60.487.

(b) An owner or operator shall include the following information in the initial semiannual report in addition to the information required in § 60.487(b)(1)–(4): number of pressure relief devices subject to the requirements of § 60.633(b) except for those pressure relief devices designated for no detectable emissions under the provisions of § 60.482–4(a) and those pressure relief devices complying with § 60.482–4(c).

(c) An owner or operator shall include the following information in all semiannual reports in addition to the information required in § 60.487(c)(2)(i)–(vi):

(1) Number of pressure relief devices for which leaks were detected as required in § 60.633(b)(2) and

(2) Number of pressure relief devices for which leaks were not repaired as required in § 60.633(b)(3).

(Approved by the Office of Management and Budget under control number 2060–0120)

3. By revising paragraphs (a) (34), (35), (36), and (40) of § 60.17 of Subpart A—General Provisions to read as follows:

§ 60.17 Incorporation by reference.

(a) * * *

(34) ASTM E169–63 (Reapproved 1977), General Techniques of Ultraviolet Quantitative Analysis, IBR approved for § 60.485(d), § 60.593(b), and § 60.632(f).

(35) ASTM E168–67 (Reapproved 1977), General Techniques of Infrared Quantitative Analysis, IBR approved for § 60.485(d), § 60.593(b), and § 60.632(f).

(36) ASTM E260–73, General Gas Chromatography Procedures, IBR approved for § 60.485(d), § 60.593(b), and § 60.632(f).

(40) ASTM D86–78, Distillation of Petroleum Products, IBR approved for § 60.593(d) and § 60.633(h).

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NESHAPS REGULATIONS

Subpart F—National Emission Standard for Vinyl Chloride [28]

§ 61.60 Applicability.

(a) This subpart applies to plants which produce:

(1) Ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene,

(2) Vinyl chloride by any process, and/or

(3) One or more polymers containing any fraction of polymerized vinyl chloride.

(b) This subpart does not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of no more than 0.19 m^3 (50 gal).

(c) Sections of this subpart other than §§ 61.61; 61.64 (a)(1), (b), (c), and (d); 61.67; 61.68; 61.69; 61.70; and 61.71 do not apply to equipment used in research and development if the reactor used to polymerize the vinyl chloride processed in the equipment has a capacity of greater than 0.19 m^3 (50 gal) and no more than 4.07 m^3 (1100 gal).[38]

§ 61.61 Definitions.

Terms used in this subpart are defined in the Act, in Subpart A of this part, or in this section as follows:

(a) "Ethylene dichloride plant" includes any plant which produces ethylene dichloride by reaction of oxygen and hydrogen chloride with ethylene.

(b) "Vinyl chloride plant" includes any plant which produces vinyl chloride by any process.

(c) "Polyvinyl chloride plant" includes any plant where vinyl chloride alone or in combination with other materials is polymerized.

(d) "Slip gauge" means a gauge which has a probe that moves through the gas/liquid interface in a storage or transfer vessel and indicates the level of vinyl chloride in the vessel by the physical state of the material the gauge discharges.

(e) "Type of resin" means the broad classification of resin referring to the basic manufacturing process for producing that resin, including, but not limited to, the suspension, dispersion, latex, bulk, and solution processes.

(f) "Grade of resin" means the subdivision of resin classification which describes it as a unique resin, i.e., the most exact description of a resin with no further subdivision.

(g) "Dispersion resin" means a resin manufactured in such away as to form fluid dispersions when dispersed in a plasticizer or plasticizer/diluent mixtures.

(h) "Latex resin" means a resin which is produced by a polymerization process which initiates from free radical catalyst sites and is sold undried.

(i) "Bulk resin" means a resin which is produced by a polymerization process in which no water is used.

(j) "Inprocess wastewater" means any water which, during manufacturing or processing, comes into direct contact with vinyl chloride or polyvinyl chloride or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product containing vinyl chloride or polyvinyl chloride but which has not been discharged to a wastewater treatment process or discharged untreated as wastewater.

(k) "Wastewater treatment process" includes any process which modifies characteristics such as BOD, COD, TSS, and pH, usually for the purpose of meeting effluent guidelines and standards; it does not include any process the purpose of which is to remove vinyl chloride from water to meet requirements of this subpart.

(l) "In vinyl chloride service" means that a piece of equipment contains or contacts either a liquid that is at least 10 percent by weight vinyl chloride or a gas that is at least 10 percent by volume vinyl chloride.

(m) "Standard operating procedure" means a formal written procedure officially adopted by the plant owner or operator and available on a routine basis to those persons responsible for carrying out the procedure.

(n) "Run" means the net period of time during which an emission sample is collected.

(o) "Ethylene dichloride purification" includes any part of the process of ethylene dichloride production which follows ethylene dichloride formation and in which finished ethylene dichloride is produced.

(p) "Vinyl chloride purification" includes any part of the process of vinyl chloride production which follows vinyl chloride formation and in which finished vinyl chloride is produced.

(q) "Reactor" includes any vessel in which vinyl chloride is partially or totally polymerized into polyvinyl chloride.

(r) "Reactor opening loss" means the emissions of vinyl chloride occurring when a reactor is vented to the atmosphere for any purpose other than an emergency relief discharge as defined in § 61.65(a).

(s) "Stripper" includes any vessel in which residual vinyl chloride is removed from polyvinyl chloride resin, except bulk resin, in the slurry form by the use of heat and/or vacuum. In the case of bulk resin, stripper includes any vessel which is used to remove residual vinyl chloride from polyvinyl chloride resin immediately following the polymerization step in the plant process flow.

(t) "Standard temperature" means a temperature of 20° C (69° F).[38]

(u) "Standard pressure" means a pressure of 760 mm of Hg (29.92 in. of Hg).[38]

§ 61.62 Emission standard for ethylene dichloride plants.[38]

(a) Ethylene dichloride purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in ethylene dichloride purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(b) Oxychlorination reactor: Except as provided in § 61.65(a), emissions of vinyl chloride to the atmosphere from each oxychlorination reactor are not to exceed 0.2 g/kg (0.0002 lb/lb) of the 100 percent ethylene dichloride product from the oxyehlorination process.

§ 61.63 Emission standard for vinyl chloride plants.

An owner or operator of a vinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) Vinyl chloride formation and purification: The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from any equipment used in vinyl chloride formation and/or purification is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

§ 61.64 Emission standard for polyvinyl chloride plants.

An owner or operator of a polyvinyl chloride plant shall comply with the requirements of this section and § 61.65.

(a) *Reactor.* The following requirements apply to reactors:

(1) The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each reactor is not to exceed 10 ppm, except as provided in paragraph (a)(2) of this section and § 61.65(a).

(2) The reactor opening loss from each reactor is not to exceed 0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride/lb) of polyvinyl chloride product, with the product determined on a dry solids basis. This requirement applies to any vessel which is used as a reactor or as both a reactor and a stripper. In the bulk process, the product means the gross product of prepolymerization and postpolymerization.

(3) Manual vent valve discharge: Except for an emergency manual vent valve discharge, there is to be no discharge to the atmosphere from any manual vent valve on a polyvinyl chloride reactor in vinyl chloride service. An emergency manual vent valve discharge means a discharge to the atmosphere which could not have been avoided by taking measures to prevent the discharge. Within 10

days of any discharge to the atmosphere from any manual vent valve, the owner or operator of the source from which the discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) *Stripper.* The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each stripper is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(c) *Mixing, weighing, and holding containers.* The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each mixing, weighing, or holding container in vinyl chloride service which precedes the stripper (or the reactor if the plant has no stripper) in the plant process flow is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(d) *Monomer recovery system.* The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each monomer recovery system is not to exceed 10 ppm, except as provided in § 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in § 61.65(b)(6)(i) before being opened.

(e) *Sources following the stripper(s).* The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper(s) [or the reactor(s) if the plant has no stripper(s)] in the plant process flow including but not limited to, centrifuges, concentrators, blend tanks, filters, dryers, conveyor air discharges, baggers, storage containers, and inprocess wastewater:

(1) In polyvinyl chloride plants using stripping technology to control vinyl chloride emissions, the weighted average residual vinyl chloride concentration in all grades of polyvinyl chloride resin processed through the stripping operation on each calendar day, measured immediately after the stripping operation is completed, may not exceed:

(i) 2000 ppm for polyvinyl chloride dispersion resins, excluding latex resins;

(ii) 400 ppm for all other polyvinyl chloride resins, including latex resins, averaged separately for each type of resin; or

(2) In polyvinyl chloride plants controlling vinyl chloride emissions with technology other than stripping or in addition to stripping, emissions of vinyl chloride to the atmosphere may not exceed:

(i) 2 g/kg (0.002 lb/lb) product from the stripper(s) [or reactor(s) if the plant has no stripper(s)] for dispersion polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis;

(ii) 0.4 g/kg (0.0004 lb/lb) product from the strippers [or reactor(s) if the plant has no stripper(s)] for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis.

§ 61.65 Emission standard for ethylene dichloride, vinyl chloride and polyvinyl chloride plants.

An owner or operator of an ethylene dichloride, vinyl chloride, and/or polyvinyl chloride plant shall comply with the requirements of this section.

(a) *Relief valve discharge.* Except for an emergency relief discharge, there is to be no discharge to the atmosphere from any relief valve on any equipment in vinyl chloride service. An emergency relief discharge means a discharge which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any relief valve discharge, the owner or operator of the source from which the relief valve discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

(b) *Fugitive emission sources.* (1) *Loading and unloading lines:* Vinyl chloride emissions from loading and unloading lines in vinyl chloride service which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows: [38]

(i) After each loading or unloading operation and before opening a loading or unloading line to the atmosphere, the quantity of vinyl chloride in all parts of each loading or unloading line that are to be opened to the atmosphere is to be reduced so that the parts combined contain no greater than 0.0038 m^3 (0.13 ft^3) of vinyl chloride, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from a loading or unloading line in accordance with paragraph (b)(1)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(2) *Slip gauges.* During loading or unloading operations, the vinyl chloride emissions from each slip gauge in vinyl chloride service are to be minimized by ducting any vinyl chloride discharged from the slip gauge through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(3) Leakage from pump, compressor, and agitator seals:

(i) *Rotating pumps.* Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing sealless pumps, pumps with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(ii) *Reciprocating pumps.* Vinyl chloride emissions from seals on all reciprocating pumps in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in § 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(iii) *Rotating compressor.* Vinyl chloride emissions from seals on all rotating compressors in vinyl chloride service are to be minimized by installing compressors with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(iv) *Reciprocating compressors.* Vinyl chloride emissions from seals on all reciprocating compressors in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in § 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(v) *Agitator.* Vinyl chloride emissions from seals on all agitators in vinyl chloride service are to be minimized by in-

stalling agitators with double mechanical seals, or equivalent as provided in § 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the agitated vessel; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(4) *Leakage from relief valves.* Vinyl chloride emissions due to leakage from each relief valve on equipment in vinyl chloride service are to be minimized by installing a rupture disk between the equipment and the relief valve, by connecting the relief valve discharge to a process line or recovery system, or equivalent as provided in § 61.66.

(5) *Manual venting of gases.* Except as provided in § 61.64(a)(3), all gases which are manually vented from equipment in vinyl chloride service are to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in § 61.66.

(6) *Opening of equipment.* Vinyl chloride emissions from opening of equipment (including loading or unloading lines that are not opened to the atmosphere after each loading or unloading operation) are to be minimized as follows:

(i) Before opening any equipment for any reason, the quantity of vinyl chloride is to be reduced so that the equipment contains no more than 2.0 percent by volume vinyl chloride or 0.0950 m^3 (25 gal) of vinyl chloride, whichever is larger, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from the equipment in accordance with paragraph (b)(6)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(7) *Samples.* Unused portions of samples containing at least 10 percent by weight vinyl chloride are to be returned to the process, and sampling techniques are to be such that sample containers in vinyl chloride service are purged into a closed process system.

(8) *Leak detection and elimination.* Vinyl chloride emissions due to leaks from equipment in vinyl chloride service are to be minimized by instituting and implementing a formal leak detection and elimination program. The owner or operator shall submit a description of the program to the Administrator for approval. The program is to be submitted within 45 days of the effective date of these regulations, unless a waiver of compliance is granted under § 61.11. If a waiver of compliance is granted, the program is to be submitted on a date scheduled by the Administrator. Approval of a program will be granted by the Administrator provided he finds:

(i) It includes a reliable and accurate vinyl chloride monitoring system for detection of major leaks and identification of the general area of the plant where a leak is located. A vinyl chloride monitoring system means a device which obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromatography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an equivalent or alternative method.

(ii) It includes a reliable and accurate portable hydrocarbon detector to be used routinely to find small leaks and to pinpoint the major leaks indicated by the vinyl chloride monitoring system. A portable hydrocarbon detector means a device which measures hydrocarbons with a sensitivity of at least 10 ppm and is of such design and size that it can be used to measure emissions from localized points.

(iii) It provides for an acceptable calibration and maintenance schedule for the vinyl chloride monitoring system and portable hydrocarbon detector. For the vinyl chloride monitoring system, a daily span check is to be conducted with a concentration of vinyl chloride equal to the concentration defined as a leak according to paragraph (b)(8)(vi) of this section. The calibration is to be done with either:

(A) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or[38]

(B) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in section 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.[38]

(iv) The location and number of points to be monitored and the frequency of monitoring provided for in the program are acceptable when they are compared with the number of pieces of equipment in vinyl chloride service and the size and physical layout of the plant.

(v) It contains an acceptable plan of action to be taken when a leak is detected.

(vi) It contains a definition of leak which is acceptable when compared with the background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system. Measurements of background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system are to be included with the description of the program. The definition of leak for a given plant may vary among the different areas within the plant and is also to change over time as background concentrations in the plant are reduced.

(9) *Inprocess wastewater.* Vinyl chloride emissions to the atmosphere from inprocess wastewater are to be reduced as follows:

(i) The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 ppm vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream is to be reduced to no more than 10 ppm by weight before being mixed with any other inprocess wastewater stream which contains less than 10 ppm vinyl chloride; before being exposed to the atmoshere; before being discharged to a wastewater treatment process; or before being discharged untreated as a wastewater. This paragraph does apply to water which is used to displace vinyl chloride from equipment before it is opened to the atmosphere in accordance with § 61.64(a)(2) or paragraph (b)(6) of this section, but does not apply to water which is used to wash out equipment after the equipment has already been opened to the atmosphere in accordance with § 61.64(a)(2) or paragraph (b)(6) of this section.[39]

(ii) Any vinyl chloride removed from the inprocess wastewater in accordance with paragraph (b)(9)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in § 61.66.

(c) The requirements in paragraphs (b)(1), (b)(2), (b)(5), (b)(6), (b)(7) and (b)(8) of this section are to be incorporated into a standard operating procedure, and made available upon request for inspection by the Administrator. The standard operating procedure is to include provisions for measuring the vinyl chloride in equipment ≥4.75 m^3 (1,250 gal) in volume for which an emission limit is prescribed in § 61.65(b)(6)(i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement is to meet the requirements in § 61.67(g)(5)(i)(A) or (g)((5)(i)(B).[39]

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)).[46,47]

§ 61.66 Equivalent equipment and procedures.

Upon written application from an owner or operator, the Administrator may approve use of equipment or procedures which have been demonstrated to his satisfaction to be equivalent in terms of reducing vinyl chloride emissions to the atmosphere to those prescribed for compliance with a specific paragraph of this subpart. For an existing source, any request for using an equivalent method as the initial measure of control is to be submitted to the Administrator within 90 days of the effective date. For a new source, any request for using an equivalent method is to be submitted to the Administrator with the application for approval of construction or modification required by § 61.07.

§ 61.67 Emission tests.

(a) Unless a waiver of emission testing is obtained under § 61.13, the owner or operator of a source to which this subpart applies shall test emissions from the source,

(1) Within 90 days of the effective date in the case of an existing source or a new source which has an initial startup date preceding the effective date, or

(2) Within 90 days of startup in the case of a new source, initial startup of which occurs after the effective date.

(b) The owner or operator shall provide the Administrator at least 30 days prior notice of an emission test to afford the Administrator the opportunity to have an observer present during the test.

(c) Any emission test is to be conducted while the equipment being tested is operating at the maximum production rate at which the equipment will be operated and under other relevant conditions as may be specified by the Administrator based on representative performance of the source.

(d) [Reserved][38]

(e) When at all possible, each sample is to be analyzed within 24 hours, but in no case in excess of 72 hours of sample collection. Vinyl chloride emissions are to be determined within 30 days after the emission test. The owner or operator shall report the determinations to the Administrator by a registered letter dispatched before the close of the next business day following the determination.[38]

(f) The owner or operator shall retain at the plant and make available, upon request, for inspection by the Administrator, for a minimum of 2 years records of emission test results and other data needed to determine emissions.

(g) Unless otherwise specified, the owner or operator shall use test Test Methods in Appendix B to this part for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an equivalent method or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

Whenever Test Method 107 is specified, and the conditions in Section 1.1, "Applicability" of Method 107A are met, Method 107A may be used.[71]

(1) Test Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in §§ 61.62(a) or (b) § 61.63(a), or §§ 61.64(a)(1), (b), (c), or (d), or from any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii).

(i) For each run, one sample is to be collected. The sampling site is to be at least two stack or duct diameters downstream and one half diameter upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. For a rectangular cross section an equivalent diameter is to be determined from the following equation:

$$\text{equivalent diameter} = 2\frac{(\text{length})\ (\text{width})}{\text{length} + \text{width}}$$

The sampling point in the duct is to be at the centroid of the cross section. The sample is to be extracted at a rate proportional to the gas velocity at the sampling point. The sample is to be taken over a minimum of one hour, and is to contain a minimum volume of 50 liters corrected to standard conditions.

(ii) Each emission test is to consist of three runs. For the purpose of determining emissions, the average of results of all runs is to apply. The average is to be computed on a time weighted basis.[38]

(iii) For gas streams containing more than 10 percent oxygen the concentration of vinyl chloride as determined by Test Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

$$C_{b\,(\text{corrected})} = C_b\frac{10.9}{20.9 - \text{percent } O_2}$$

where:

$C_{b\,(\text{corrected})}$ = The concentration of vinyl chloride in the exhaust gases, corrected to 10-percent oxygen.
C_b = The concentration of vinyl chloride as measured by Test Method 106.
20.9 = Percent oxygen in the ambient air at standard conditions.
10.9 = Percent oxygen in the ambient air at standard conditions, minus the 10.0-percent oxygen to which the correction is being made.
Percent O_2 = Percent oxygen in the exhaust gas as measured by Reference Method 3 in Appendix A of Part 60 of this chapter.[38]

(iv) For those emission sources where the emission limit is prescribed in terms of mass rather than concentration, mass emissions in kg/100 kg product are to be determined by using the following equation:

$$C_{BX} = \frac{[C_b(2.60)\,Q\ 10^{-6}]\ [100]}{Z}$$

where:

C_{BX} = kg vinyl chloride/100 kg product.
C_b = The concentration of vinyl chloride as measured by Test Method 106.
2.60 = Density of vinyl chloride at one atmosphere and 20° C in kg/m³.
Q = Volumetric flow rate in m³/hr as determined by Reference Method 2 of Appendix A to Part 60 of this chapter.
10^{-6} = Conversion factor for ppm.
Z = Production rate (kg/hr).[38]

(2) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in § 61.65(b)(9)(i).

(3) Where a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined using Test Method 107 as follows:

(i) The number of strippers and samples and the types and grades of resin to be sampled are to be determined by the Administrator for each individual plant at the time of the test based on the plant's operation.

(ii) Each sample is to be taken immediately following the stripping operation.

(iii) The corresponding quantity of material processed by each stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraph (g)(3)(i) of this section.

(4) Where control technology other than or in addition to a stripping operation is used to attain the emission limit in § 61.64(e), emissions are to be determined as follows:

(i) Test Method 106 is to be used to determine atmospheric emissions from all of the process equipment simultaneously. The requirements of paragraph (g)(1) of this section are to be met.

(ii) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream subject to the emission limit prescribed in § 61.64(e). The mass of vinyl chloride in kg/100 kg product in each in process wastewater stream is to be determined by using the following equation:

$$C_{BX} = \frac{[C_A R\ 10^{-6}]\ [100]}{Z}$$

where:

C_{BX} = kg vinyl chloride/100 kg product.
C_A = the concentration of vinyl chloride as measured by Test Method 107.
R = water flow rate in l/hr, determined in accordance with a method which has been submitted to and approved by the Administrator.
10^{-6} = Conversion factor for ppm.
Z = Production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the Administrator.

(5) The reactor opening loss for which an emission limit is prescribed in § 61.64(a)(2) is to be determined. The number of reactors for which the determination

is to be made is to be specified by the Administrator for each individual plant at the time of the determination based on the plant's operation. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

(i) Except as provided in paragraph (g)(5)(ii) of this section, the reactor opening loss is to be determined using the following equation:

$$C = \frac{W\ (2.60)\ (10^{-4})\ (Cb)}{YZ}$$

where:

C = kg vinyl chloride emissions/kg product.
W = Capacity of the reactor in m^3.
2.60 = Density of vinyl chloride at one atmosphere and 20° C in kg/m^3.
10^{-4} = Conversion factor for ppm.
Cb = ppm by volume vinyl chloride as determined by Test Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppm.
Y = Number of batches since the reactor was last opened to the atmosphere.
Z = Average kg of polyvinyl chloride produced per batch in the number of batches since the reactor was last opened to the atmosphere.

(A) If Method 106 is used to determine the concentration of vinyl chloride (Cb), the sample is to be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole. Samples are to be taken for 5 minutes within 6 inches of the vessel bottom, 5 minutes near the vessel center, and 5 minutes near the vessel top.

(B) If a portable hydrocarbon detector is used to determine the concentration of vinyl chloride (Cb), a probe of sufficient length to reach the vessel bottom from the manhole is to be used to make the measurements. One measurement will be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements are to be made at each location until the reading is stabilized. All hydrocarbons measured are to be assumed to be vinyl chloride.

(C) The production rate of polyvinyl chloride (Z) is to be determined by a method submitted to and approved by the Administrator.

(ii) A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the Administrator as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)). [46,47]

§ 61.68 Emission monitoring.

(a) A vinyl chloride monitoring system is to be used to monitor on a continuous basis the emissions from the sources for which emission limits are prescribed in § 61.62(a) and (b), § 61.63(a), and § 61.64(a)(1), (b), (c), and (d), and for any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.65 (b)(1)(ii), and (b)(2), (b)(5), (b)(6)(ii), and (b)(9)(ii).[30]

(b) The vinyl chloride monitoring system(s) used to meet the requirement in paragraph (a) of this section is to be a device which obtains air sampels from one or more points on a continuous sequential basis and analyzes the samples with gas chromotography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an equivalent or alternative method. The vinyl chloride monitoring system used to meet the requirements in § 61.65(b)(8)(i) may be used to meet the requirements of this section.

(c) A daily span check is to be conducted for each vinyl chloride monitoring system used. For all of the emission sources listed in paragraph (a) of this section, except the one for which an emission limit is prescribed in § 61.62(b), the daily span check is to be concducted with a concentration of vinyl chloride equal to 10 ppm. For the emission source for which an emission limit is prescribed in § 61.62(b), the daily span check is to be conducted with a concentration of vinyl chloride which is determined to be equivalent to the emission limit for that source based on the emission test required by § 61.67. The calibration is to be done with either:

(1) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or[38]

(2) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in sections 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.[38]

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)). [46,47]

§ 61.69 Initial report.

(a) An owner or operator of any source to which this subpart applies shall submit a statement in writing notifying the Administrator that the equipment and procedural specifications in § 61.65 (b)(1), (b)(2), (b)(3), (b)(4), (b)(5), (b)(6), (b)(7), and (b)(8) are being implemented.

(b)(1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the effective date, unless a waiver of compliance is granted under § 61.11, along with the information required under § 61.10. If a waiver of compliance is granted, the statement is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the initial startup date.

(c) The statement is to contain the following information:

(1) A list of the equipment installed for compliance,

(2) A description of the physical and functional characteristics of each piece of equipment.

(3) A description of the methods which have been incorporated into the standard operating procedures for measuring or calculating the emissions for which emission limits are prescribed in § 61.65 (b)(1)(i) and (b)(6)(i),

(4) A statement that each piece of equipment is installed and that each piece of equipment and each procedure is being used.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)). [46,47]

§ 61.70 Semiannual report.

(a) The owner or operator of any source to which this subpart applies shall submit to the Administrator on September 15 and March 15 of each year a report in writing containing the information required by this section. The first semiannual report is to be submitted following the first full 6 month reporting period after the initial report is submitted.[30]

(b)(1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the effective date, unless a waiver of compliance is granted under § 61.11. If a waiver of compliance is granted, the first report is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the initial startup date.

(c) Unless otherwise specified, the owner or operator shall use the Test Methods in Appendix B to this part to conduct emission tests as required by paragraphs (c)(2) and (c)(3) of this section, unless an equivalent or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use

of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(1) The owner or operator shall include in the report a record of any emissions which averaged over any hour period (commencing on the hour) are in excess of the emission limits prescribed in §§ 61.62(a) or (b), § 61.63(a), or § 61.64(a)(1), (b), (c), or (d), or for any control system to which reactor emissions are required to be ducted in § 61.64(a)(2) or to which fugitive emissions are required to be ducted in § 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii). The emissions are to be measured in accordance with § 61.68.

(2) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in § 61.64(e), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin. Test Method 107 is to be used to determine vinyl chloride content as follows:

(i) If batch stripping is used, one representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping operation, and identified by resin type and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.[38]

(ii) If continuous stripping is used, one representative sample of polyvinyl chloride resin is to be taken for each grade of resin processed or at intervals of 8 hours for each grade of resin which is being processed, whichever is more frequent. The sample is to be taken as the resin flows out of the stripper and identified by resin type and grade and the date and time the sample was taken. The corresponding quantity of material processed by each stripper over the time period represented by the sample during the eight hour period, is to be recorded and identified by resin type and grade and the date and time it represents.

(iii) The quantity of material processed by the stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section.

(v) The report to the Administrator by the owner or operator is to include the vinyl chloride content found in each sample required by paragraphs (c)(2)(i) and (c)(2)(ii) of this section, averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$A_{T_i} = \frac{\sum_{j=1}^{n} P_{G_j} M_{G_j}}{Q_{T_i}} = \frac{P_{G_1} M_{G_1} + P_{G_2} M_{G_2} + \cdots + P_{G_n} M_{G_n}}{Q_{T_i}}$$

where:

A = 24-hour average concentration of type T_i resin in ppm (dry weight basis).
Q = Total production of type T_i resin over the 24-hour period, in kg.
T_i = Type of resin; $i = 1, 2 \ldots m$ where m is total number of resin types produced during the 24-hour period.
M = Concentration of vinyl chloride in one sample of grade G_i resin, in ppm.
P = Production of grade G_i resin represented by the sample, in kg.
G_i = Grade of resin; e.g., G_1, G_2, and G_3.
n = Total number of grades of resin produced during the 24-hour period.[38]

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 2 years records of all data needed to furnish the information required by paragraph (c)(2)(v) of this section: The records are to contain the following information:

(A) The vinyl chloride content found in all the samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section, identified by the resin type and grade and the time and date of the sample, and

(B) The corresponding quantity of polyvinyl chloride resin processed by the stripper(s), identified by the resin type and grade and the time and date it represents.

(3) The owner or operator shall include in the report a record of the emissions from each reactor opening for which an emission limit is prescribed in § 61.64(a)(2). Emissions are to be determined in accordance with § 61.67(g)(5), except that emissions for each reactor are to be determined. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)). [46,47]

§ 61.71 Recordkeeping.

(a) The owner or operator of any source to which this subpart applies shall retain the following information at the source and make it available for inspection by the Administrator for a minimum of two years:

(1) A record of the leaks detected by the vinyl chloride monitoring system, as required by § 61.65(b)(8), including the concentrations of vinyl chloride measured, analyzed, and recorded by the vinyl chloride detector, the location of each measurement and the date and approximate time of each measurement.

(2) A record of the leaks detected during routine monitoring with the portable hydrocarbon detector and the action taken to repair the leaks, as required by § 61.65(b)(8), including a brief statement explaining the location and cause of each leak detected with the portable hydrocarbon detector, the date and time of the leak, and any action taken to eliminate that leak.[38]

(3) A record of emissions measured in accordance with § 61.68.[38]

(4) A daily operating record for each polyvinyl chloride reactor, including pressures and temperatures.[38]

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414)). [46,47]

38 FR 8826, 4/6/73 (1)

as amended

41 FR 46560, 10/21/76 (28)
41 FR 53017, 12/3/76 (30)
42 FR 29005, 6/7/77 (38)
42 FR 41424, 8/17/77 (40)
43 FR 8800, 3/3/78 (47)
47 FR 39485, 9/8/82 (71)

Subpart J—National Emission Standard for Equipment Leaks (Fugitive Emission Sources) of Benzene [97]

§ 61.110 Applicability and designation of sources.

(a) The provisions of this subpart apply to each of the following sources that are intended to operate in benzene service: pumps, compressors, pressure relief devices, sampling connections, systems, open-ended valves or lines, valves, flanges and other connectors, product accumulator vessels, and control devices or systems required by this subpart.

(b) The provisions of this subpart do not apply to sources located in coke by-product plants.

(c)(1) If an owner or operator applies for one of the exemptions in this paragraph, then the owner or operator shall maintain records as required in § 61.246(i).

(2) Any equipment in benzene service that is located at a plant site designed to produce or use less than 1,000 megagrams of benzene per year is exempt from the requirements of § 61.112.

(3) Any process unit (defined in § 61.241) that has no equipment in benzene service is exempt from the requirements of § 61.112.

(d) While the provisions of this subpart are effective, a source to which this subpart applies that is also subject to the provisions of 40 CFR Part 60 only will be required to comply with the provisions of this subpart.

§ 61.111 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act, in Subpart A of Part 61, or in Subpart V of Part 61, and the following terms shall have the specific meanings given them:

"In benzene service" means that a piece of equipment either contains or contacts a fluid (Liquid or gas) that is at least 10 percent benzene by weight as determined according to the provisions of § 61.245(d). The provisions of § 61.245(d) also specify how to determine that a piece of equipment is not in benzene service.

"Semiannual" means a 6-month period: the first semiannual period concludes on the last day of the last month during the 180 days following initial startup for new sources; and the first semiannual period concludes on the last day of the last full month during the 180 days after June 6, 1984 for existing sources.

§ 61.112 Standards.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the requirements of Subpart V of this part.

(b) An owner or operator may elect to comply with the requirements of § 61.243–1 and § 61.243–2.

(c) An owner or operator may apply to the Administrator for a determination of an alternative means of emission limitation that achieves a reduction in emissions of benzene at least equivalent to the reduction in emissions of benzene achieved by the controls required in this subpart. In doing so, the owner or operator shall comply with requirements of § 61.244.

§ 61.113–61.119 [Reserved]

38 FR 8826, 4/6/73 (1)

as amended

49 FR 23498, 6/6/84 (97)

Subpart V—National Emission Standard for Equipment Leaks (Fugitive Emission Sources)[97]

§ 61.240 Applicability and designation of sources.

(a) The provisions of this subpart apply to each of the following sources that are intended to operate in volatile hazardous air pollutant (VHAP) service: pumps, compressors, pressure relief devices, sampling connection systems, open-ended valves or lines, valves, flanges and other connectors, product accumulator vessels, and control devices or systems required by this subpart.

(b) The provisions of this subpart apply to the sources listed in paragraph (a) after the date of promulgation of a specific subpart in Part 61.

(c) While the provisions of this subpart are effective, a source to which this subpart applies that is also subject to the provisions of 40 CFR Part 60 only will be required to comply with the provisions of this subpart.

§ 61.241 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act, in Subpart A of Part 61, or in specific subparts of Part 61; and the following terms shall have specific meaning given them:

"Closed-vent system" means a system that is not open to atmosphere and that is composed of piping, connections, and, if necessary, flow-inducing devices that transport gas or vapor from a piece or pieces of equipment to a control device.

"Connector" means, flanged, screwed, welded, or other joined fittings used to connect two pipe lines or a pipe line and a piece of equipment.

"Control device" means an enclosed combustion device, vapor recovery system, or flare.

"Double block and bleed system" means two block valves connected in series with a bleed valve or line that can vent the line between the two block valves.

"Equipment" means each pump, compressor, pressure relief device, sampling connection system, open-ended valve or line, valve, flange or other connector, product accumulator vessel in VHAP service, and any control devices or systems required by this subpart.

"First attempt at repair" means to take rapid action for the purpose of stopping or reducing leakage of organic material to atmosphere using best practices.

"In gas/vapor service" means that a piece of equipment contains process fluid that is in the gaseous state at operating conditions.

"In liquid service" means that a piece of equipment is not in gas/vapor service.

"*In-situ* sampling systems" means nonextractive samplers or in-line samplers.

"In vacuum service" means that equipment is operating at an internal pressure which is at least 5 kilopascals (kPa) below ambient pressure.

"In VHAP service" means that a piece of equipment either contains or contacts a fluid (liquid or gas) that is at least 10 percent by weight a volatile hazardous air pollutant (VHAP) as determined according to the provisions of § 61.245(d). The provisions of § 61.245(d) also specify how to determine that a piece of equipment is not in VHAP service.

"In VOC service" means, for the purposes of this subpart, that (a) the piece of equipment contains or contacts a process fluid that is at least 10 percent VOC by weight (see 40 CFR 60.2 for the definition of volatile organic compound or VOC and 40 CFR 60.485(d) to determine whether a piece of equipment is not in VOC service) and (b) the piece of equipment is not in liquid service as defined in 40 CFR 60.481.[112]

"Open-ended valve or line" means any valve, except pressure relief valves, having one side of the valve seat in contact with process fluid and one side open to atmosphere, either directly or through open piping.

"Pressure release" means the emission of materials resulting from the system pressure being greater than the set pressure of the pressure relief device.

"Process unit" means equipment assembled to produce a VHAP or its derivatives as intermediates or final products, or equipment assembled to use a VHAP in the production of a product. A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient product storage facilities.

"Process unit shutdown" means a work practice or operational procedure that stops production from a process unit or part of a process unit. An unscheduled work practice or operational procedure that stops production from a process unit or part of a process unit for less than 24 hours is not a process unit shutdown. The use of spare equipment and technically feasible bypassing of equipment without stopping production are not process unit shutdowns.

"Product accumulator vessel" means any distillate receiver, bottoms receiver, surge control vessel, or product separator in VHAP service that is vented to atmosphere either directly or through a vacuum-producing system. A product accumulator vessel is in VHAP service if the liquid or the vapor in the vessel is at least 10 percent by weight VHAP.

"Repaired" means that equipment is adjusted, or otherwise altered, to eliminate a leak as indicated by one of the following: an instrument reading of 10,000 ppm or greater, indication of liquids dripping, or indication by a sensor that a seal or barrier fluid system has failed.

"Semiannual" means a 6-month period; the first semiannual period concludes on the last day of the last month during the 180 days following initial startup for new sources; and the first semiannual period concludes on the last day of the last full month during the 180 days after the effective date of a specific subpart that references this subpart for existing sources.[112]

"Sensor" means a device that measures a physical quantity or the change in a physical quantity, such as temperature, pressure, flow rate, pH, or liquid level.

"Volatile Hazardous Air Pollutant" or "VHAP" means a substance regulated under this subpart for which a standard for equipment leaks of the substance has been proposed and promulgated. Benzene is a VHAP.

§ 61.242-1 Standards: General.

(a) Each owner or operator subject to the provisions of this subpart shall demonstrate compliance with the requirements of § 61.242-1 to § 61.242-11 for each new and existing source as required in 40 CFR 61.05, except as provided in § 61.243 and § 61.244.

(b) Compliance with this subpart will be determined by review of records, review of performance test results, and inspection using the methods and procedures specified in § 61.245.

(c)(1) An owner or operator may request a determination of alternative means of emission limitation to the requirements of §§ 61.242-2, 61.242-3, 61.242-5, 61.242-6, 61.242-7, 61.242-8, 61.242-9 and 61.242-11 as provided in § 61.244.[112]

(2) If the Administrator makes a determination that a means of emission limitation is at least a permissible alternative to the requirements of §§ 61.242-2, 61.242-3, 61.242-5, 61.242-6, 61.242-7, 61.242-8, 61.242-9 or 61.242-11,

an owner or operator shall comply with the requirements of that determination.

(d) Each piece of equipment to which this subpart applies shall be marked in such a manner that it can be distinguished readily from other pieces of equipment.

(e) Equipment that is in vacuum service is excluded from the requirements of § 61.242–2, to § 61.242–11 if it is identified as required in § 61.246(e)(5).

§ 61.242–2 Standards: Pumps.

(a)(1) Each pump shall be monitored monthly to detect leaks by the methods specified in § 61.245(b), except as provided in § 61.242–1(c) and paragraphs (d), (e), and (f) of this section.

(2) Each pump shall be checked by visual inspection each calendar week for indications of liquids dripping from the pump seal.

(b)(1) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(2) If there are indications of liquids dripping from the pump seal, a leak is detected.

(c)(1) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 61.242–10.

(2) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(d) Each pump equipped with a dual mechanical seal system that includes a barrier fluid system is exempt from the requirements of pargraph (a), provided the following requirements are met:

(1) Each dual mechanical seal system is:

(i) Operated with the barrier fluid at a pressure that is at all times greater than the pump stuffing box pressure; or

(ii) Equipped with a barrier fluid degassing reservior that is connected by a closed-vent system to a control device that complies with the requirements of § 61.242–11; or

(iii) Equipped with a system that purges the barrier fluid into a process stream with zero VHAP emissions to atmosphere.

(2) The barrier fluid is not in VHAP service and, if the pump is covered by standards under 40 CFR Part 60, is not in VOC service.

(3) Each barrier fluid system is equipped with a sensor that will detect failure of the seal system, the barrier fluid system, or both.

(4) Each pump is checked by visual inspection each calendar week for indications of liquids dripping from the pump seal.

(5)(i) Each sensor as described in paragraph (d)(3) of this section is checked daily or is equipped with a audible alarm, and

(ii) The owner or operator determines, based on design considerations and operating experience, a criterion that indicates failure of the seal system, the barrier fluid system, or both.

(6)(i) If there are indications of liquids dripping from the pump seal or the sensor indicates failure of the seal system, the barrier fluid system, or both based on the criterion determined in paragraph (d)(5)(ii), a leak is detected.

(ii) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 61.242–10.

(iii) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(e) Any pump that is designated, as described in § 61.246(e)(2), for no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, is exempt from the requirements of paragraphs (a), (c), and (d) if the pump:

(1) Has no externally actuated shaft penetrating the pump housing.

(2) Is demonstrated to be operating with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as measured by the method specified in § 61.245(c), and

(3) Is tested for compliance with paragraph (e)(2) initially upon designation, annually, and at other times requested by the Administrator.

(f) If any pump is equipped with a closed-vent system capable of capturing and transporting any leakage from the seal or seals to a control device that complies with the requirements of § 61.242–11, it is exempt from the requirements of paragraphs (a)–(e).

(g) Any pump that is located within the boundary of an unmanned plant site is exempt from the weekly visual inspection requirement of paragraphs (a)(2) and (d)(4) of this section, and the daily requirements of paragraph (d)(5)(i) of this section, provided that each pump is visually inspected as often as practicable and at least monthly.[112]

§ 61.242–3 Standards: Compressors.

(a) Each compressor shall be equipped with a seal system that includes a barrier fluid system and that prevents leakage of process fluid to atmosphere, except as provided in § 61.242–1(c) and paragraphs (h) and (i) of this section.

(b) Each compressor seal system as required in paragraph (a) shall be:

(1) Operated with the barrier fluid at pressure that is greater than the compressor stuffing box pressure; or

(2) Equipped with a barrier fluid system that is connected by a closed-vent system to a control device that complies with the requirements of § 61.242–11; or

(3) Equipped with a system that purges the barrier fluid into a process stream with zero VHAP emissions to atmosphere.

(c) The barrier fluid shall not be in VHAP service and, if the compressor is covered by standards under 40 CFR Part 60, shall not be in VOC service.

(d) Each barrier fluid system as described in paragraphs (a)–(c) of this section shall be equipped with a sensor that will detect failure of the seal system, barrier fluid system, or both.

(e)(1) Each sensor as required in paragraph (d) of this section shall be checked daily or shall be equipped with an audible alarm unless the compressor is located within the boundary of an unmanned plant site.[112]

(2) The owner or operator shall determine, based on design considerations and operating experience, a criterion that indicates failure of the seal system, the barrier fluid system, or both.

(f) If the sensor indicates failure of the seal system, the barrier fluid system, or both based on the criterion determined under paragraph (e)(2) of this section, a leak is detected.

(g)(1) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 61.242–10.

(2) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(h) A compressor is exempt from the requirements of paragraphs (a) and (b) if it is equipped with a closed-vent system capable of capturing and transporting any leakage from the seal to a control device that complies with the requirements of § 61.242–11, except as provided in paragraph (i).

(i) Any Compressor that is designated, as described in § 61.246(e)(2), for no detectable emission as indicated by an instrument reading of less than 500 ppm above background is exempt from the

requirements of paragraphs (a)–(h) if the compressor:

(1) Is demonstrated to be operating with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as measured by the method specified in § 61.245(c); and

(2) Is tested for compliance with paragraph (i)(1) initially upon designation, annually, and at other times requested by the Administrator.

§ 61.242–4 Standards: Pressure relief devices in gas/vapor service.

(a) Except during pressure releases, each pressure relief device in gas/vapor service shall be operated with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as measured by the method specified in § 61.245(c).

(b)(1) After each pressure release, the pressure relief device shall be returned to a condition of no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as soon as practicable, but no later than 5 calendar days after each pressure release, except as provided in § 61.242–10.[112]

(2) No later than 5 calendar days after the pressure release, the pressure relief device shall be monitored to confirm the condition of no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, as measured by the method specified in § 61.245(c).

(c) Any pressure relief device that is equipped with a closed-vent system capable of capturing and transporting leakage from the pressure relief device to a control device as described in § 61.242–11 is exempt from the requirements of paragraphs (a) and (b).

§ 61.242–5 Standards: Sampling connecting systems.

(a) Each sampling connection system shall be equipped with a closed-purge system or closed vent system, except as provided in § 61.242–1(c).

(b) Each closed-purge system or closed-vent system as required in paragraph (a) shall:

(1) Return the purged process fluid directly to the process line with zero VHAP emissions to atmosphere; or

(2) Collect and recycle the purged process fluid with zero VHAP emissions to atmosphere; or

(3) Be designed and operated to capture and transport all the purged process fluid to a control device that complies with the requirements of § 61.242–11.

(c) *In-situ* sampling systems are exempt from the requirements of paragraphs (a) and (b).

§ 61.242–6 Standards: Open-ended valves or lines.

(a)(1) Each open-ended valve or line shall be equipped with a cap, blind flange, plug, or a second valve, except as provided in § 61.242–1(c).

(2) The cap, blind flange, plug, or second valve shall seal the open end at all times except during operations requiring process fluid flow through the open-ended valve or line.

(b) Each open-ended valve or line equipped with a second valve shall be operated in a manner such that the valve on the process fluid end is closed before the second valve is closed.

(c) When a double block and bleed system is being used, the bleed valve or line may remain open during operations that require venting the line between the block valves but shall comply with paragraph (a) at all other times.

§ 61.242–7 Standards: Valves.

(a) Each valve shall be monitored monthly to detect leaks by the method specified in § 61.245(b) and shall comply with paragraphs (b)–(e), except as provided in paragraphs (f), (g), and (h) of this section, §§ 61.243–1 or 61.243–2, and § 61.242–1(c).

(b) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(c)(1) Any valve for which a leak is not detected for 2 successive months may be monitored the first month of every quarter, beginning with the next quarter, until a leak is detected.

(2) If a leak is detected, the valve shall be monitored monthly until a leak is not detected for 2 successive months.

(d)(1) When a leak is detected, it shall be repaired as soon as practicable, but no later than 15 calendar days after the leak is detected, except as provided in § 61.242–10.

(2) A first attempt at repair shall be made no later than 5 calendar days after each leak is detected.

(e) First attempts at repair include, but are not limited to, the following best practices where practicable:

(1) Tightening of bonnet bolts;

(2) Replacement of bonnet bolts;

(3) Tightening of packing gland nuts; and

(4) Injection of lubricant into lubricated packing.

(f) Any valve that is designated, as described in § 61.246(e)(2), for no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, is exempt from the requirements of paragraph (a) if the valve:

(1) Has no external actuating mechanism in contact with the process fluid;

(2) Is operated with emissions less than 500 ppm above background, as measured by the method specified in § 61.245(c); and

(3) Is tested for compliance with paragraph (f)(2) initially upon designation, annually, and at other times requested by the Administrator.

(g) Any valve that is designated, as described in § 61.246(f)(1), as an unsafe-to-monitor valve is exempt from the requirements of paragraph (a) if:

(1) The owner or operator of the valve demonstrates that the valve is unsafe to monitor because monitoring personnel would be exposed to an immediate danger as a consequence of complying with paragraph (a); and

(2) The owner or operator of the valve has a written plan that requires monitoring of the valve as frequent as practicable during safe-to-monitor times.

(h) Any valve that is designated, as described in § 61.246(f)(2), as a difficult-to-monitor valve is exempt from the requirements of paragraph (a) if:

(1) The owner or operator of the valve demonstrates that the valve cannot be monitored without elevating the monitoring personnel more than 2 meters above a support surface;

(2) The process unit within which the valve is located is an existing process unit; and

(3) The owner or operator of the valve follows a written plan that requires monitoring of the valve at least once per calendar year.

§ 61.242–8 Standards: Pressure relief devices in liquid service and flanges and other connectors.

(a) Pressure relief devices in liquid service and flanges and other connectors shall be monitored within 5 days by the method specified in § 61.245(b) if evidence of a potential leak is found by visual, audible, olfactory, or any other detection method, except as provided in § 61.242–1(c).[112]

(b) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(c)(1) When a leak is detected, it shall be repaired as soon as practicable, but not later than 15 calendar days after it is detected, except as provided in § 61.242–10.

(2) The first attempt at repair shall be made no later than 5 calendar days after

each leak is detected.

(d) First attempts at repair include, but are not limited to, the best practices described under § 61.242-7(e).

§ 61.242-9 Standards: Product accumulator vessels.

Each product accumulator vessel shall be equipped with a closed-vent system capable of capturing and transporting any leakage from the vessel to a control device as described in § 61.242-11, except as provided in § 61.242-1(c). [112]

§ 61.242-10 Standards: Delay of repair.

(a) Delay of repair of equipment for which leaks have been detected will be allowed if the repair is technically infeasible without a process unit shutdown. Repair of this equipment shall occur before the end of the next process unit shutdown.

(b) Delay of repair of equipment for which leaks have been detected will be allowed for equipment that is isolated from the process and that does not remain in VHAP service.

(c) Delay of repair for valves will be allowed if:

(1) The owner or operator demonstrates that emissions of purged material resulting from immediate repair are greater than the fugitive emissions likely to result from delay of repair, and

(2) When repair procedures are effected, the purged material is collected and destroyed or recovered in a control device complying with § 61.242-11.

(d) Delay of repair for pumps will be allowed if:

(1) Repair requires the use of a dual mechanical seal system that includes a barrier fluid system, and

(2) Repair is completed as soon as practicable, but not later than 6 months after the leak was detected.

(e) Delay of repair beyond a process unit shutdown will be allowed for a valve if valve assembly replacement is necessary during the process unit shutdown, valve assembly supplies have been depleted, and valve assembly supplies had been sufficiently stocked before the supplies were depleted. Delay of repair beyond the next process unit shutdown will not be allowed unless the next process unit shutdown occurs sooner than 6 months after the first process unit shutdown.

§61.242-11 Standards: Closed-vent systems and control devices.

(a) Owners or operators of closed-vent systems and control devices used to comply with provisions of this subpart shall comply with the provisions of this section, except as provided in § 61.242-1(c). [112]

(b) Vapor recovery systems (for example, condensers and adsorbers) shall be designed and operated to recover the organic vapors vented to them with an efficiency of 95 percent or greater.

(c) Enclosed combustion devices shall be designed and operated to reduce the VHAP emissions vented to them with an efficiency of 95 percent or greater or to provide a minimum residence time of 0.50 seconds at a minimum temperature of 760°C.

(d)(1) Flares shall be designed for an operated with no visible emissions as determined by the methods specified in § 61.245(e), except for periods not to exceed a total of 5 minutes during any 2 consecutive hours. [112]

(2) Flares shall be operated with a flame present at all times, as determined by the methods specified in § 61.245.(e).

(3) Flares shall be used only with the net heating value of the gas being combusted being 11.2 MJ/scm (300 Btu/scf) or greater if the flare is steam-assisted or air-assisted; or with the net heating value of the gas being combusted being 7.45 MJ/scm or greater if the flare is nonassisted. The net heating value of the gas being combusted shall be determined by the method specified in § 61.245(e).

(4) Steam-assisted and nonassisted flares shall be designed for and operated with an exit velocity, as determined by the method specified in § 61.245(e)(4), less than 18 m/sec (60 ft/sec).

(5) Air-assisted flares shall be designed and operated with an exit velocity less than the velocity, v_{max}, as determined by the method specified in § 61.245(e)(5).

(6) Flares used comply with this subpart shall be steam-assisted, air-assisted, or nonassisted.

(e) Owners or operators of control devices that are used to comply with the provisions of this supbart shall monitor these control devices to ensure that they are operated and maintained in conformance with their design.

(f)(1) Closed-vent systems shall be designed for and operated with no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background and by visual inspections, as determined by the methods specified as § 61.245(c).

(2) Closed-event systems shall be monitored to determine compliance with this section initially in accordance with § 61.05, annually, and at other times requested by the administrator.

(3) Leaks, as indicated by an instrument reading greater than 500 ppm and visual inspections, shall be repaired as soon as practicable, but not later than 15 calendar days after the leak is detected.

(4) A first attempt at repair shall be made no later than 5 calendar days after the leak is detected.

(g) Closed-vent systems and control devices use to comply with provisions of this subpart shall be operated at all times when emissions may be vented to them.

§ 61.243-1 Alternative standards for valves in VHAP service—allowable percentage of valves leaking.

(a) An owner or operator may elect to have all valves within a process unit to comply with an allowable percentage of valves leaking of equal to or less than 2.0 percent.

(b) The following requirements shall be met if an owner or operator decides to comply with an allowable percentage of valves leaking:

(1) An owner or operator must notify the Administrator that the owner or operator has elected to have all valves within a process unit to comply with the allowable percentage of valves leaking before implementing this alternative standard, as specified in § 61.247(d).

(2) A performance test as specified in paragraph (c) of this section shall be conducted initially upon designation, annually, and at other times requested by the Administrator.

(3) If a valve leak is detected, it shall be repaired in accordance with § 61.242-7(d) and (e).

(c) Performance tests shall be conducted in the following manner:

(1) All valves in VHAP service within the process unit shall be monitored within 1 week by the methods specified in § 61.245(b).

(2) If an instrument reading of 10,000 ppm or greater is measured, a leak is detected.

(3) The leak percentage shall be determined by dividing the number of valves in VHAP service for which leaks are detected by the number of valves in VHAP service within the process unit.

(d) Owner or operators who elect to have all valves comply with this alternative standard shall not have a process unit with a leak percentage greater than 2.0 percent.

(e) If an owner or operator decides no longer to comply with § 61.243-1, the owner or operator must notify the Administrator in writing that the work practice standard described in § 61.242-7(a)-(e) will be followed.

§ 61.243–2 Alternative standards for valves in VHAP service—skip period leak detection and repair.

(a)(1) An owner or operator may elect for all valves within a process unit to comply with one of the alternative work practices specified in paragraphs (b)(2) and (3) of this section.

(2) An owner or operator must notify the Administrator before implementing one of the alternative work practices, as specified in § 61.247(d).

(b)(1) An owner or operator shall comply initially with the requirements for valves, as described in § 61.242–7.

(2) After 2 consecutive quarterly leak detection periods with the percentage of valves leaking equal to or less than 2.0, an owner or operator may begin to skip 1 of the quarterly leak detection periods for the valves in VHAP service.

(3) After 5 consecutive quarterly leak detection periods with the percentage of valves leaking equal to or less than 2.0, an owner or operator may begin to skip 3 of the quartely leak detection periods for the valves in VHAP service.

(4) If the percentage of valves leaking is greater than 2.0, the owner or operator shall comply with the requirements as described in § 61.242–7 but may again elect to use this section.

§ 61.244 Alternative means of emission limitation.

(a) Permission to use an alternative means of emission limitation under Section 112(e)(3) of the Clean Air Act shall be governed by the following procedures:

(b) Where the standard is an equipment, design, or operational requirement:

(1) Each owner or operator applying for permission shall be responsible for collecting and verifying test data for an alternative means of emission limitation.

(2) The Administrator will compare test data for the means of emission limitation to test data for the equipment, design, and operational requirements.

(3) The Administrator may condition the permission on requirements that may be necessary to assure operation and maintenance to achieve the same emission reduction as the equipment, design, and operational requirements.

(c) Where the standard is a work practice:

(1) Each owner or operator applying for permission shall be responsible for collecting and verifying test data for an alternative means of emission limitation.

(2) For each source for which permission is requested, the emission reduction achieved by the required work practices shall be demonstrated for a minimum period of 12 months.

(3) For each source for which permission is requested, the emission reduction achieved by the alternative means of emission limitation shall be demonstrated.

(4) Each owner or operator applying for permission shall commit in writing each source to work practices that provide for emission reductions equal to or greater than the emission reductions achieved by the required work practices.

(5) The Administrator will compare the demonstrated emission reduction for the alternative means of emission limitation to the demonstrated emission reduction for the required work practices and will consider the commitment in paragraph (c)(4).

(6) The Administrator may condition the permission on requirements that may be necessary to assure operation and maintenance to achieve the same emission reduction as the required work practices of this subpart.

(d) An owner or operator may offer a unique approach to demonstrate the alternative means of emission limitation.

(e)(1) Manufacturers of equipment used to control equipment leaks of a VHAP may apply to the Administrator for permission for an alternative means of emission limitation that achieves a reduction in emissions of the VHAP achieved by the equipment, design, and operational requirements of this subpart.

(2) The Administrator will grant permission according to the provisions of paragraphs (b), (c), and (d).

§ 61.245 Test methods and procedures.

(a) Each owner or operator subject to the provisions of this subpart shall comply with the test methods and procedures requirements provided in this section.

(b) Monitoring, as required in § 61.242, § 61.243, and § 61.244, shall comply with the following requirements:

(1) Monitoring shall comply with Reference Method 21.

(2) The detection instrument shall meet the performance criteria of Reference Method 21.

(3) The instrument shall be calibrated before use on each day of its use by the procedures specified in Reference Method 21.

(4) Calibration gases shall be:

(i) Zero air (less than 10 ppm of hydrocarbon in air); and [1,2]

(ii) A mixture of methane or n-hexane and air at a concentration of approximately, but less than, 10,000 ppm methane or n-hexane.

(5) The instrument probe shall be traversed around all potential leak interfaces as close to the interface as possible as described in Reference Method 21.

(c) When equipment is tested for compliance with no detectable emissions, as required in §§ 61.242–2(e), 61.242–3(i), 61.242–4, 61.242–7(f), and 61.242–11(f), the test shall comply with the following requirements:

(1) The requirements of paragraphs (b)(1)–(4) shall apply.

(2) The background level shall be determined, as set forth in Reference Method 21.

(3) The instrument probe shall be traversed around all potential leak interfaces as close to the interface as possible as described in Reference Method 21.

(4) The arithmetic difference between the maximum concentration indicated by the instrument and the background level is compared with 500 ppm for determining compliance.[1,2]

(d)(1) Each piece of equipment within a process unit that can conceivably contain equipment in VHAP service is presumed to be in VHAP service unless an owner or operator demonstrates that the piece of equipment is not in VHAP service. For a piece of equipment to be considered not in VHAP service, it must be determined that the percent VHAP content can be reasonably expected never to exceed 10 percent by weight. For purposes of determining the percent VHAP content of the process fluid that is contained in or contacts equipment, procedures that conform to the methods described in ASTM Method D–2267 (incorporated by the reference as specified in § 61.18) shall be used.

(2)(i) An owner or operator may use engineering judgment rather than the procedures in paragraph (d)(1) of this section to demonstrate that the percent VHAP content does not exceed 10 percent by weight, provided that the engineering judgment demonstrates that the VHAP content clearly does not exceed 10 percent by weight. When an owner or operator and the Administrator do not agree on whether a piece of equipment is not in VHAP service, however, the procedures in paragraph (d)(1) of this section shall be used to resolve the disagreement.

(ii) If an owner or operator determines that a piece of equipment is in VHAP service, the determination can be revised only after following the procedures in paragraph (d)(1) of this section.

(3) Samples used in determining the percent VHAP content shall be representative of the process fluid that is contained in or contacts the equipment or the gas being combusted in the flare.

(e)(1) Reference Method 22 shall be

used to determine compliance of flares with the visible emission provisions of this subpart.

(2) The presence of a flare pilot flame shall be monitored using a thermocouple or any other equivalent device to detect the presence of a flame.

(3) The net heating value of the gas being combusted in a flare shall be calculated using the following equation:

$$H_T = K \left(\sum_{i=1}^{n} C_i H_i \right)$$

Where:

H_T = Net heating value of the sample. MJ/scm; where the net enthalpy per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C.

K = Constant, 1.74×10^{-7} (1/ppm) (g mole/scm) (MJ/kcal) where standard [113] temperature for (g mole/scm) is 20°C

C_i = Concentration of sample component i in ppm, as measured by Reference Method 18 of Appendix A of 40 FR Part 60 and ASTM D2504–67 (reapproved 1977) (incorporated by reference as specified in § 61.18).

H_i = Net heat of combustion of sample component i, kcal/g mole. The heats of combustion may be determined using ASTM D2382–76 (incorporated by reference as specified in § 61.18) if published values are not available or cannot be calculated

(4) The actual exit velocity of a flare shall be determined by dividing the volumetric flowrate (in units of standard temperature and pressure), as determined by Reference Method 2, 2A, 2C, or 2D, as appropriate, by the unobstructed (free) cross section area of the flare tip.

(5) The maximum permitted velocity, V_{max}, for air-assisted flares shall be determined by the following equation:

$VMax = 8.706 + 0.7084(H_T)$

Where:

VMax = Maximum permitted velocity, m/sec

8.706 = Constant.

0.7084 = Constant.

H_T = The net heating value as determined in paragraph (e)(3) of this section.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414).)

§ 61.246 Recordkeeping requirements.

(a)(1) Each owner or operator subject to the provisions of this subpart shall comply with the recordkeeping requirements of this section.

(2) An owner or operator of more than one process unit subject to the provisions of this subpart may comply with the recordkeeping requirements for these process units in one recordkeeping system if the system identifies each record by each process unit.

(b) When each leak is detected as specified in §§ 61.242–2, 61.242–3, 61.242–7, and 61.242–8, the following requirements apply:

(1) A weatherproof and readily visible identification, marked with the equipment identification number, shall be attached to the leaking equipment.

(2) The identification on a valve may be removed after it has been monitored for 2 successive months as specified in § 61.242–7(c) and no leak has been detected during those 2 months.

(3) The identification on equipment, except on a valve, may be removed after it has been repaired.

(c) When each leak is detected as specified in §§ 61.242–2, 61.242–3, 61.242–7, and 61.242–8, the following information shall be recorded in a log and shall be kept for 2 years in a readily accessible location:

(1) The instrument and operator identification numbers and the equipment identification number.

(2) The date the leak was detected and the dates of each attempt to repair the leak.

(3) Repair methods applied in each attempt to repair the leak.

(4) "Above 10,000" if the maximum instrument reading measured by the methods specified in § 61.245(a) after each repair attempt is equal to or greater than 10,000 ppm.

(5) "Repair delayed" and the reason for the delay if a leak is not repaired within 15 calendar days after discovery of the leak.

(6) The signature of the owner or operator (or designate) whose decision it was that repair could not be effected without a process shutdown.

(7) The expected date of successful repair of the leak if a leak is not repaired within 15 calendar days.

(8) Dates of process unit shutdowns that occur while the equipment is unrepaired.

(9) The date of successful repair of the leak.

(d) The following information pertaining to the design requirements for closed-vent systems and control devices described in § 61.242–11 shall be recorded and kept in a readily accessible location:

(1) Detailed schematics, design specifications, and piping and instrumentation diagrams.

(2) The dates and descriptions of any changes in the design specifications.

(3) A description of the parameter or parameters monitored, as required in § 61.242–11(e), to ensure that control devices are operated and maintained in conformance with their design and an explanation of why that parameter (or parameters) was selected for the monitoring.

(4) Periods when the closed-vent systems and control devices required in §§ 61.242–2, 61.242–3, 61.242–4, 61.242–5 and 61.242–9 are not operated as designed, including periods when a flare pilot light does not have a flame.

(5) Dates of startups and shutdowns of the closed-vent systems and control devices required in §§ 61.242–2, 61.242–3, 61.242–4, 61.242–5 and 61.242–9.

(e) The following information pertaining to all equipment subject to the requirements in § 61.242–1 to § 61.242–11 shall be recorded in a log that is kept in a readily accessible location:

(1) A list of identification numbers for equipment (except welded fittings) subject to the requirements of this subpart.[112]

(2)(i) A list of identification numbers for equipment that the owner or operator elects to designate for no detectable emissions, as indicated by an instrument reading of less than 500 ppm above background, under the provisions of §§ 61.242–2(e), 61.242–3(i), and 61.242–7(f).

(ii) The designation of this equipment as subject to the requirements of § 61.242–2(e), 61.242–3(i), or 61.242–7(f) shall be signed by the owner or operator.

(3) A list of equipment identification numbers for pressure relief devices required to comply with § 61.242–4(a).

(4)(i) The dates of each compliance test required in §§ 61.242–2(e), 61.242–3(i), 61.242–4, and 61.242–7(f).

(ii) The background level measured during each compliance test.

(iii) The maximum instrument reading measured at the equipment during each compliance test.

(5) A list of identification numbers for equipment in vacuum service.

(f) The following information pertaining to all valves subject to the requirements of § 61.242–7(g) and (h) shall be recorded in a log that is kept in a readily accessible location:

(1) A list of identification numbers for valves that are designated as unsafe to monitor, an explanation for each valve stating why the valve is unsafe to monitor, and the plan for monitoring each valve.

(2) A list of identification numbers for valves that are designated as difficult to monitor, an explanation for each valve

stating why the valve is difficult to monitor, and the planned schedule for monitoring each valve.

(g) The following information shall be recorded for valves complying with § 61.243–2:

(1) A schedule of monitoring.

(2) The percent of valves found leaking during each monitoring period.

(h) The following information shall be recorded in a log that is kept in a readily accessible location:

(1) Design criterion required in § 61.242–2(d)(5) and § 61.242–3(e)(2) and an explanation of the design criterion; and

(2) Any changes to this criterion and the reasons for the changes.

(i) The following information shall be recorded in a log that is kept in a readily accessible location for use in determining exemptions as provided in the applicability section of this subpart and other specific subparts:

(1) An analysis demonstrating the design capacity of the process unit, and

(2) An analysis demonstrating that equipment is not in VHAP service.

(j) Information and data used to demonstrate that a piece of equipment is not in VHAP service shall be recorded in a log that is kept in a readily accessible location.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414).)

(Approved by the Office of Management and Budget under control number 2060–0068)

§ 61.247 Reporting requirements.

(a)(1) An owner or operator of any piece of equipment to which this subpart applies shall submit a statement in writing notifying the Administrator that the requirements of §§ 61.242, 61.245, 61.246, and 61.247 are being implemented.

(2) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the effective date, unless a waiver of compliance is granted under § 61.11, along with the information required under § 61.10. If a waiver of compliance is granted, the statement is to be submitted on a date scheduled by the Administrator.

(3) In the case of new sources which did not have an initial startup date preceding the effective date, the statement shall be submitted with the application for approval of construction, as described in § 61.07.

(4) The statement is to contain the following information for each source.

(i) Equipment identification number and process unit identification.

(ii) Type of equipment (for example, a pump or pipeline valve).

(iii) Percent by weight VHAP in the fluid at the equipment.

(iv) Process fluid state at the equipment (gas/vapor or liquid).

(v) Method of compliance with the standard (for example, "monthly leak detection and repair" or "equipped with dual mechanical seals").

(b) A report shall be submitted to the Administrator semiannually starting 6 months after the initial report required in § 61.247(a), that includes the following information:

(1) Process unit identification.

(2) For each month during the semiannual reporting period,

(i) Number of valves for which leaks were detected as described in § 61.242–7(b) of § 61.243–2.

(ii) Number of valves for which leaks were not repaired as required in § 61.242–7(d).

(iii) Number of pumps for which leaks were detected as described in § 61.242–2(b) and (d)(6).

(iv) Number of pumps for which leaks were not repaired as required in § 61.242–2(c) and (d)(6).

(v) Number of compressors for which leaks were detected as described in § 61.242–3(f).

(vi) Number of compressors for which leaks were not repaired as required in § 61.242–3(g).

(vii) The facts that explain any delay of repairs and, where appropriate, why a process unit shutdown was technically infeasible.

(3) Dates of process unit shutdowns which occurred within the semiannual reporting period.

(4) Revisions to items reported according to paragraph (a) if changes have occurred since the initial report or subsequent revisions to the initial report.

"[Note.—Compliance with the requirements of § 61.10(c) is not required for revisions documented under this paragraph.]."[12]

(5) The results of all performance tests to determine compliance with § 61.242–2(e), § 61.242–3(i), § 61.242–4(a), § 61.242–7(f), § 61.242–11(f), § 61.243–1 and § 61.243–2 conducted within the semiannual reporting period.

(c) In the first report submitted as required in § 61.247(a), the report shall include a reporting schedule stating the months that semiannual reports shall be submitted. Subsequent reports shall be submitted according to that schedule, unless a revised schedule has been submitted in a previous semiannual report.

(d) An owner or operator electing to comply with the provisions of §§ 61.243–1 and 61.243–2 shall notify the Administrator of the alternative standard selected 90 days before implementing either of the provisions.

(e) An application for approval of construction or modification, § 61.05(a) and § 61.07, will not be required if—

(1) The new source complies with the standard, § 61.242;

(2) The new source is not part of the construction of a process unit; and

(3) In the next semiannual report required by § 61.247(b), the information in § 61.247(a)(3) is reported.

(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414).) (Approved by the Office of Management and Budget under control number ICR–1153.)

38 FR 8826, 4/6/73 (1)

as amended

49 FR 23498, 6/6/84 (97)

APPENDIX B

ORGANIC VAPOR ANALYZER RESPONSE FACTORS

TABLE B-1. RESPONSE FACTORS FOR AID MODEL 580 AND MODEL 585 PHOTOIONIZATION TYPE ORGANIC VAPOR ANALYZERS[a] (10.0-eV Lamp)

Compound	Ionization potential, eV	Response factor
Acetone	9.58	1.7
Acetophenone	N.D.	4.2
Acrolein	N.D.	25.0
Ammonia	10.15	24.5
Aniline	7.70	0.6
Benzene	9.25	0.7
1,3 Butadiene	9.07	1.0
Carbon disulfide	10.0	2.3
Chlorobenzene	9.07	0.5
Cyclohexane	9.98	2.1
1,2-Dichloroethane	N.D.	50.0
Diethylamine	N.D.	2.0
Dimethyl sulfide	8.69	1.3
Ethyl benzene	8.75	1.7
Ethylene oxide	10.57	33.8
Ethyl ether	9.53	1.5
Hexane	10.18	11.3
Hydrogen sulfide	10.45	7.3
Isopropanol	10.16	19.8
Methyl ethyl ketone	9.53	1.6
Methyl isocyanate	10.57	12.5
Methyl mercaptan	9.4	1.3
Methyl methacrylate	N.D.	4.2
Nitric oxide	9.25	44.9
Ortho chloro toluene	8.83	0.5
Ortho xylene	8.56	0.8
Pyridine	9.32	0.6
Styrene	N.D.	3.3
Sec butyl bromide	9.98	1.7
Tetrachloroethene	9.32	1.6
Tetrachloroethylene	N.D.	1.9
Tetrahydrofuran	9.54	3.7
Toluene	8.82	0.5
Trichloroethylene	N.D.	1.3

[a]Source: Reference 9.

TABLE B-2. RESPONSE FACTORS FOR THE MIRAN MODEL 1A/80 INFRARED ANALYZER[a]

Compound	Wavelength, μm	Actual concentration, ppmv	Instrument concentration, ppmv	Response factor
Acetal	9.5	1,000	6,690	0.149
		5,000	23,400	0.214
		10,000	27,200	0.368
Acetyl-1-propanol, 3-	3.3	500	247	2.02
		1,000	813	1.23
	9.5	100	39	2.55
		500	217	2.30
		1,000	406	2.46
Benzoyl chloride	6.35	100	4,870	0.02
		500	5,080	0.10
		1,000	5,420	0.19
Carbon tetrachloride	5.7	500	115	4.35
		1,000	232	4.31
		10,000	390	25.6
Chloro-acetaldehyde	6.35	500	4,840	0.103
		1,000	5,680	0.176
		10,000	6,760	1.48
	9.5	500	76	6.58
		1,000	228	4.39
		10,000	1,880	5.32
	13.5	500	709	0.705
		1,000	2,300	0.435
		10,000	21,800	0.459
Chloroform	13.5	1,000	6,680	0.150
		5,000	22,200	0.225
		10,000	34,200	0.292
Dichloro-1-propanol,2,3-	3.3	1,200	64.9	18.5
Diisopropyl Benzene,1,3-	6.35	500	134	3.75
		1,225	507	2.42
	5.7	100	311	0.331
		500	343	1.47
		1,225	380	3.22
Diketene	3.3	5,000	354	14.1
		10,000	1,240	8.06

(continued)

TABLE B-2 (continued)

Compound	Wavelength, μm	Actual concentration, ppmv	Instrument concentration, ppmv	Response factor
	5.7	1,000	2,280	0.439
		5,000	6,390	0.782
		10,000	8,600	1.16
	9.5	1,000	69.4	14.4
		5,000	377	13.4
		10,000	580	17.2
Dimethylsulfide	5.7	1,000	822	1.22
		5,000	1,010	4.95
		10,000	1,180	8.47
	6.35	1,000	2,480	0.403
		5,000	4,590	1.09
		10,000	6,540	1.53
	9.5	1,000	15.3	65.4
		5,000	120	41.7
		10,000	270	37.0
Ethanol	3.3	1,000	3,830	0.261
		5,000	18,500	0.270
		10,000	34,300	0.292
	3.4	1,000	430	2.33
		5,000	3,420	1.46
		10,000	7,530	1.33
Ethylene glycol dimethyl ether	3.3	1,000	5,110	0.196
		5,000	21,100	0.237
		10,000	33,800	0.296
	3.4	1,000	2,310	0.433
		5,000	11,700	0.427
		10,000	20,600	0.485
	3.6	1,000	284	3.52
		5,000	1,870	2.67
		10,000	3,920	2.55
Ethylene glycol monoethyl ether acetate	3.6	1,000	50.8	19.7
		2,000	158	12.7
	5.7	200	2,590	0.0772
		1,000	5,110	0.196
		2,000	6,960	0.287

(continued)

TABLE B-2 (continued)

Compound	Wave-length, μm	Actual concentration, ppmv	Instrument concentration, ppmv	Response factor
	8.8	1,000	261	3.83
		2,000	808	2.48
	9.5	200	472	0.424
		1,000	2,190	0.457
		2,000	3,470	0.576
Formaldehyde	3.3	500	266	1.88
		1,000	916	1.09
	3.4	1,000	72.4	13.8
Formic acid	5.7	500	4,990	0.100
		5,000	23,600	0.212
		10,000	31,300	0.319
	8.8	5,000	1,000	5.00
		10,000	2,920	3.42
	9.5	500	1,190	0.420
		5,000	9,120	0.548
		10,000	14,100	0.709
Freon 12	6.35	1212.5	5,940	0.204
		2,425	6,470	0.375
		4,850	7,490	0.648
	8.8	1212.5	1,714	0.707
		2,425	3,130	0.775
		4,850	4,680	1.04
Furfural	13.5	100	656	0.152
		500	5,470	0.0914
		1,200	12,200	0.0984
Glycidol	3.3	100	262	0.382
	3.6	100	572	0.175
	5.7	100	3,100	0.323
	6.35	100	6,540	0.0153
	9.5	1,000	132	0.758
Hydroxyacetone	5.7	100	1,950	0.0513

(continued)

TABLE B-2 (continued)

Compound	Wave-length, μm	Actual concentration, ppmv	Instrument concentration, ppmv	Response factor
	6.35	100	6,870	0.0146
	9.5	100	24.6	4.07
Methyl styrene, -	3.3	1,030	976	1.06
		5,000	2,830	1.77
	5.7	103	330	0.312
		1,030	1,230	0.837
		5,000	1,570	3.18
	6.35	1,010	4,490	0.229
		5,000	6,960	0.718
	9.5	1,030	73.6	14.0
		5,000	178	28.1
	13.5	1,030	167	6.17
		5,000	948	5.27
Methylene chloride	3.3	5,000	1,740	2.87
		10,000	3,740	2.67
Pentanethiol,1-	13.5	5,000	5,300	0.943
		10,000	10,500	0.952
Perchloromethyl-mercaptan	3.3	5,000	612	8.17
	3.6	5,000	64.0	78.1
	5.7	500	1,730	0.289
		1,000	3,410	0.293
		5,000	7,660	0.653
	8.8	5,000	426	11.7
	9.5	500	36.7	13.6
		1,000	132	7.58
		5,000	303	16.5
Propylene chlorohydrin	13.5	500	3,800	0.132
		1,000	8,510	0.118
		5,000	38,600	0.130

(continued)

TABLE B-2 (continued)

Compound	Wavelength, μm	Actual concentration, ppmv	Instrument concentration, ppmv	Response factor
Tetrachloroethane, 1,1,2,1-	3.3	5,000	582	8.59
		10,000	1,010	9.90
	8.8	10,000	404	24.8
	13.8	1,000	20,000	0.0500
		5,000	73,000	0.0685
		10,000	101,000	0.0990
Trichloroethane,1,1,1-	3.3	1,000	266	3.76
		5,000	2,910	1.72
		10,000	5,920	1.69
	3.4	5,000	38.8	129.0
		10,000	421	23.8
Trichlorotrifluoroethane, 1,1,2-	8.8	1,000	5,840	0.171
		5,000	16,100	0.311
		10,000	18,500	0.541
	9.5	1,000	977	1.02
		5,000	3,690	1.36
		10,000	6,280	1.59
	13.5	5,000	1,100	4.55
		10,000	2,270	4.41

[a]Abstracted from Reference 8.

TABLE B-3. RESPONSE FACTORS FOR THE HNU SYSTEMS, INC., MODEL PI-101 PHOTOIONIZATION ANALYZER[a]

Compound	Actual concentration	Instrument concentration	Response factor
Acetal	1,000	925	1.1
	5,000	7,200	0.69
	10,000	13,200	0.76
Carbon disulfide	1,000	1,990	0.50
	10,000	12,900	0.78
Carbon tetrachloride	500	784	0.64
	1,000	1,070	0.94
	10,000	6,070	1.6
Chloroform	1,000	756	1.3
	5,000	2,550	2.0
	10,000	5,250	1.9
Diketene	1,000	148	6.8
	5,000	318	16.0
	10,000	460	22.0
Perchloromethyl mecaptan	5,000	103	48.0
Toluene	1,000	1,180	0.85
Tetrachloroethane,1,1,2,2-	1,000	736	1.4
	5,000	1,170	4.3
	10,000	1,880	5.3
Trichloroethane,1,1,	1,000	1,020	0.98
	5,000	6,170	0.81
	10,000	9,430	1.1
Trichlorotrifluoroethane 1,1,2-	5,000	155	32.0
	10,000	430	23.0

[a]Abstracted from Reference 8.

TABLE B-4. RESPONSE FACTORS FOR FOXBORO OVA-108 AND BACHARACH TLV SNIFFER AT 10,000 ppmv RESPONSE[a]

Compound	Response factor OVA-108[b]	Response factor TLV sniffer[b]
Acetic acid	1.64	15.60
Acetic ahydride	1.39	5.88
Acetone	0.80	1.22
Acetonitrile	0.95	1.18
Acetyl chloride	2.04	2.72
Acetylene	0.39	B
Acrylic acid	4.59	B
Acrylonitrile	0.97	3.49 I
Allene	0.64	15.00
Allyl alcohol	0.96	X
Amylene	0.44	1.03
Anisole	0.92	3.91
Benzene	0.29	1.07
Bromobenzene	0.40	1.19
Butadiene, 1,3-	0.57	10.90
Butane, N	1.44 I	4.11
Butanol, sec-	0.76	1.25
Butanol, tert	0.53	2.17
Butene, 1-	0.56	5.84
Butyl acetate	0.66	1.38
Butyl acrylate, N-	0.70	2.57 I
Butyl ether, N	2.60	3.58 I
Butyl ether, sec	0.35	1.15
Butylamine, N	0.69	2.02
Butylamine, sec	0.70	1.56
Butylamine, tert-	0.63	1.95
Butyraldehyde, N-	1.29	2.30
Butyronitrile	0.52	1.47 I
Carbon disulfide	B	3.92
Chloroacetaldehyde	9.10	5.07
Chlorobenzene	0.38	0.88
Chloroethane	5.38 I	3.90 P
Chloroform	9.28	B
Chloropropene, 1-	0.67	0.87
Chloropropene, 3-	0.80	1.24
Chlorotoluene, M-	0.48	0.91
Chlorotoluene, O-	0.48	1.06
Chlorotoluene, P-	0.56	1.17 I
Crotonaldehyde	1.25	B
Cumene	1.87	B
Cyclohexane	0.47	0.70
Cychohexanone	1.50	7.04
Cyclohexene	0.49	2.17
Cyclohexylamine	0.57	1.38
Diacetyl	1.54	3.28

(continued)

TABLE B-4 (continued)

Compound	Response factor OVA-108[b]	Response factor TLV sniffer[b]
Dichloro-1-propene,2,3-	0.75	1.75
Dichloroethane, 1,1-	0.78	1.86
Dichloroethane,1,2-	0.95	2.15
Dichloroethylene,cis,1,2-	1.27	1.63
Dichloroethylene,trans,1,1-	1.11	1.66
Dichloromethane	2.81	3.85
Dichloropropane,1,2-	1.03	1.54
Diisobutylene	0.35	1.41
Dimethoxy ethane,1,2-	1.22	1.52
Dimethylformamide,N,N-	4.19	5.29
Dimethylhydrazine,1,1-	1.03	2.70
Dioxane	1.48	1.31
Epichlorohydrin	1.69	2.03
Ethane	0.65	0.69 I
Ethanol	1.78	X
Ethoxy ethanol, 2-	1.55	1.82
Ethyl acetate	0.86	1.43
Ethyl acrylate	0.77	X
Ethyl chloroacetate	1.99	1.59
Ethyl ether	0.97	1.14
Ethylbenzene	0.73	4.74 D
Ethylene	0.71	1.56
Ethylene oxide	2.46	2.40
Ethylenediamine	1.73	3.26
Formic acid	14.20	B
Glycidol	6.88	5.55
Heptane	0.41 I	0.73
Hexane,N-	0.41	0.69
Hexene,1-	0.49	4.69 D
Hydroxyacetone	6.90	15.20
Isobutane	0.41	0.55
Isobutylene	3.13	B
Isoprene	0.59	X
Isopropanol	0.91	1.39
Isopropyl acetate	0.71	1.31
Isopropyl chloride	0.68	0.98
Isovaleraldehyde	0.64	2.19 D
Mesityl oxide	1.09	3.14
Methacrolein	1.20	3.49 D
Methanol	4.39 P	2.01
Methoxy-ethanol,2-	2.25	3.13
Methyl acetate	1.74	1.85
Methyl acetylene	0.61	6.79
Methyl chloride	1.44	1.84
Methyl ethyl ketone	0.64	1.12
Methyl formate	3.11	1.94

(continued)

TABLE B-4 (continued)

Compound	Response factor OVA-108[b]	Response factor TLV sniffer[b]
Methyl methacrylate	0.99	2.42
Methyl-2-pentanol,4-	1.66	2.00
Methyl-2-pentone,4-	0.56	1.63
Methyl-3-butyn-2-ol,2	0.59	X
Methylcyclohexane	0.48	0.84
Methylcyclohexene	0.44	2.79
Methylstyrene,a-	13.90	B
Nitroethane	1.40	3.45
Nitromethane	3.52	7.60
Nitropropane	1.05	2.02
Nonane-n	1.54	11.10
Octane	1.03	2.11
Pentane	0.52	0.83
Picoline,2-	0.43	1.18
Propane	0.55 I	0.60 P
Propionaldehyde	1.14	1.71
Proponic acid	1.30	5.08 D
Propyl alcohol	0.93	1.74
Propylbenzene,n-	0.51	B
Propylene	0.77	1.74 I
Propylene oxide	0.83	1.15
Pyridine	0.47	1.16
Styrene	4.22	B
Tetrachloroethane,1,1,1,2	4.83 D	6.91
Tetrachloroethane,1,1,2,2	7.89	25.40
Tetrachloroethylene	2.97	B
Toluene	0.39	2.68 D
Trichloroethane,1,1,1-	0.80	2.40
Trichloroethane,1,1,2-	1.25	3.69
Trichloroethylene	0.95	3.93
Trichloropropane,1,2,3-	0.96	1.99
Triethylamine	0.51	1.48
Vinyl chloride	0.84	1.06
Vinylidene chloride	1.12	2.41
Xylene, p-	2.12	7.87
Xylene, m-	0.40	5.87 D
Xylene, O-	0.43	1.40

[a]Abstracted from Reference 6.

[b]I = Inverse estimation method
D = Possible outliers in data
N = Narrow range of data
X = No data available
B = 10,000 ppmv response unachievable
P = Suspect points eliminated.

APPENDIX C

IONIZATION POTENTIALS OF SELECTED ORGANIC COMPOUNDS

IONIZATION POTENTIAL DATA USEFUL FOR SELECTION OF PHOTOIONIZATION TYPE ORGANIC VAPOR ANALYZERS[a]

Chemical	Ionization potential	Chemical	Ionization potential
Acetaldehyde	10.21	3-butene nitrile	10.39
Acetamide	9.77	n-butyl acetate	10.01
Acetic acid	10.37	sec-butyl acetate	9.91
Acetone	9.69	n-butyl alcohol	10.04
Acetonitrile	12.22	n-butyl amine	8.71
Acetophenone	9.27	s-butyl amine	8.70
Acetyl bromide	10.55	t-butyl amine	8.64
Acetyl chloride	11.02	n-butly benzene	8.69
Acetylene	11.41	s-butyl benzene	8.68
Acrolein	10.10	t-butyl bnnzene	8.68
Acrylonitrile	10.91	n-butyl formate	10.50
Allyl alcohol	9.67	1-butyne	10.18
Ammonia	10.15	n-butyraldehyde	9.86
Aniline	7.70	n-butyric acid	10.16
Anisole	8.22	n-butyronitrile	11.67
Benzaldehyde	9.53	Carbon dioxide	13.79
Benzene	9.25	Carbon monoxide	14.01
Benzenethiol	8.33	Chlorine	11.48
Benzonitrile	9.71	Chlorobenzene	9.07
Benzotrifluoride	9.68	1-chlorobutane	10.67
Biphenyl	8.27	2-chlorobutane	10.65
Bromine	10.55	1-chloro-2-fluorobenzene	9.16
1-bromobutane	10.13	1-cholor-3-fluorobenzene	9.21
2-bromobutane	9.98	1-chloro-2-methylpropane	10.66
1-bromo-2-chloroethane	10.63	2-chloro-2-methylpropane	10.61
Bromochloromethane	10.77	1-chloropropane	10.82
1-bromo-4-fluorobenzene	8199	2-chloropropane	10.78
1-bromo-2-methylpropane	10.09	3-chloropropene	10.04
1-bromo-2-methylpropane	9.89	2-chlorothiophene	8.68
1-bromopentane	10.10	m-chlorotoluene	8.83
1-brompropane	10.18	o-chlorotoluene	8.83
2-bromopropene	10.08	p-chlorotoluene	8.70
1-bromopropene	9.30	Crotonaldehyde	9.73
3-bromopropene	9.70	Cyanogen	13.80
2-bromothiophene	8.63	Cyclohexane	9.98
m-bromotoluene	8.81	Cyclohexanone	9.14
o-bromotoluene	8.79	Cyclohexene	8.95
p-bromotolyene	8.67	Cyclo-octatetraene	7.99
Butane	10.63	Cyclopentane	10.53
1,3-butadiene	9.07	Cyclopentanone	9.01
2,3-butadione	9.23	Cyclopropane	10.06
1-butanethiol	9.14	Dedaborane	11.00
1-butene	9.58	Dibromochloromethane	10.59
cis-2-butene	9.13	Dibromodifluoromethane	11.07
Trans-2-butene	9.13	1,1 dibromoethane	10.19

1,2 dibromoethene	9.45
Dibromomethane	10.49
1,3 dibromopropane	10.07
m-dichlorobenzene	9.12
o-dichlorobenzene	9.07
p-dichlorobenzene	8.94
1,2 dichloroethane	11.12
cis-dichloroethene	9.65
trans-dichloroethene	9.66
Diborane	12.10
Dichloromethane	11.35
1,2 dichloropropane	10.87
1,3 dichloropropane	10.85
2,3 dichloropropene	9.82
Dibutyl amine	7.69
Diethoxymethane	9.70
N,N-diethyl acetamide	8.60
Diethyl amine	8.01
Diethyl ether	9.43
N,N-diethyl formamide	8.89
Diethyl ketone	9.32
Diethyl sulfide	8.43
Diethyl sulfite	9.68
Dihydropyran	8.34
1,1 dimethoxyethane	9.65
Dimethoxymethane	10.00
Diiodomethane	9.34
Diisopropylamine	7.73
N,N-dimethyl acetamide	8.81
Dimethyl amine	8.2
2,2-dimethyl butane	10.06
2,3-dimethyl butane	10.02
3,3-dimethyl butanone	9.17
Dimethyl ether	10.00
N,N-dimethyl formamide	9.12
2,2-dimethyl propane	10.35
Dimethyl sulfide	8.69
Dipropyl amine	7.84
Dipropyl sulfide	8.30
Durene	8.03
Ethane	11.65
Ethanethiol	9.29
Ethene	10.52
Ethyl acetate	10.11
Ethyl alcohol	10.48
Ethyl amine	8.86
Ethyl benzene	8.76
Ethyl bromide	10.29
Ethyl chloride	10.98
Ethyl disulfide	8.27
Ethylene oxide	10.57
Ethyl formate	10.61
Ethyl iodide	9.33
Ethyl isothiocyanate	9.14
Ethyl methyl sulfide	8.55
Ethyl nitrate	11.22
Ethyl propionate	10.00
Ethyl thiocyanate	9.89
Ethynylbenzene	8.82
Fluorine	15.70
Fluorobenzene	9.20
o-fluorophenol	8.66
m-fluorotoluene	8.92
o-fluorotolune	8.92
p-fluorotoluene	8.79
Formaldehyde	10.87
Formic acid	11.05
Freon 11 (CFC13)	11.77
Freon 12 (CF2C12)	12.91
Freon 13 (CF3C1)	12.91
Freon 22 (CHC1F2)	12.45
Freon 113 (CF3CC13)	11.78
2-furaldehyde	9.21
Furan	8.89
Hexane	10.18
Heptane	10.08
2-Heptanone	9.33
1-hexene	9.46
Hydrogen	15.43
Hydrogen bromide	11.62
Hydrogen chloride	12.74
Hydrogen cyanide	13.91
Hydrogen fluorine	15.77
Hydrogen iodide	10.38
Hydrogen sulfide	10.46
Hydrogen telluride	9.14
Iodine	9.25
Iodobenzene	8.73
1-iodobutane	9.21
2-iodobutane	9.09
1-iodo-2-methylpropane	9.18
1-iodo-2-methylpropane	9.02
1-iodopentane	9.19
1-iodopropane	9.26
2-iodopropane	9.17
o-iodotoluene	8.62
m-iodotoluene	8.61
p-iodotoluene	8.50
Isobutane	10.57
Isobutyl amine	8.70
Isobutyl acetate	9.97
Isobutyl formate	10.46
Isobutyraldehyde	9.76
Isobutyric acid	10.02
Isopentane	10.32
Isoprene	8.85
Isopropyl acetate	9.99
Isopropyl benzene	10.16
Isopropyl ether	9.20
Isovaleraldehyde	9.71

2,3-lutidine	8.85
2,4-lutidine	8.85
2,6-lutidine	8.85
Mesitylene	8.40
Mesityl oxide	9.08
Methane	12.98
Methanelthiol	9.44
N-methyl acetamide	8.90
Methyl acetate	10.27
Methyl alcohol	10.85
Methyl amine	8.97
Methyl bromide	10.53
2-methyl-1-butane	9.12
3-methyl-1-butene	9.51
3-methyl-2-butene	8.67
Methyl butyl ketone	9.34
Methyl butyrate	10.07
Methyl chloride	11.28
Methylcyclohexane	9.85
4-methylcyclohexene	8.91
Methyl disulfude	8.46
Methyl ethyl ketone	9.53
Methyl formate	10.82
2-methyl furan	8.39
Methyl iodide	9.54
Methyl isobutyl ketone	9.30
Methyl isobutyrate	9.98
Methyl isopropyl ketone	9.32
Methyl isothiocyanate	9.25
1-methyl naphthalene	7.96
2-methyl naphthalene	7.96
2-methylpentane	10.12
3-methylpentane	10.08
2-methyl propene	9.23
Methyl propionate	10.15
Methyl propyl ketone	9.39
Methyl thiocyanate	10.07
a-methyl styrene	8.35
Naphthalene	8.12
Nitric oxide	9.25
Nitrobenzene	9.92
Nitrogen	15.50
Nitrogen dioxide	9.78
Nitroethane	10.81
Nitromethane	11.00
1-nitropropane	10.88
2-nitropropane	10.71
Oxygen	12.08
Ozone	12.08
Pentaborane	10.40
Pentane	10.35
2,4 pentanedione	8.87
1-pentene	9.50
Phenetole	8.11
Phenol	8.50
Phenyl isocyanate	8.77
Phenyl isothiocyanate	8.52
Phosgene	11.77
2-picoline	9.02
3-picoline	9.02
4-picoline	9.04
Propane	11.07
1-propanethiol	9.20
Propiolactone	9.70
Propionic acid	10.24
Propionitrile	11.84
Propionaldehyde	9.98
Propyl acetate	10.04
Propyl alcohol	10.20
Propyl amine	8.72
Propyl bnezene	8.72
Propylene	9.73
Propylene oxide	10.22
Propyl ether	9.27
Propyl formate	10.54
Propylene	10.36
Pyridine	9.32
Pyrrole	8.20
Styrene	8.47
Thiolacetic acid	10.00
Thiophene	8.86
Tetrachloroethene	9.32
Tetrachloromethane	11.47
Tetrahydrofuran	9.54
Tetrahydropyran	9.26
Tolune	8.82
Tribromethene	9.27
Tribromofluoromethane	10.67
Tribromomethane	10.51
Trichloroethene	9.45
Trichloromethane	11.42
Triethylamine	7.50
Trimethyl amine	7.52
2,2,4-trimethyl pentane	9.86
Tripropyl amine	7.23
Valeraldehyde	9.82
Valeric acid	10.12
Vinyl acetate	9.19
Vinyl bromide	9.80
Vinyl chloride	10.00
Vinyl methyl ether	8.93
Water	12.59
m-xylene	8.56
o-xylene	8.56
p-xylene	8.45

[a]Source: Reference 5.

GLOSSARY

Accuracy: The difference between the measured value and the true values which has been established by an accepted reference method procedure. In most cases, a value is quoted by the manufacturer, and no description is given to indicate how this value was obtained.

Action Level: A measured concentration value obtained with a portable VOC monitor. It indicates the need for repair.

Calibration: The method for determining the instrument response to calibration gases (dynamic calibration) or artificial stimuli (static calibration).

Directed Maintenance: Refers to a maintenance procedure in which the hydrocarbon detector is used during maintenance. The leak is monitored with the instrument until the repair reduces the measured concentration below the action level.

Fugitive Emissions of VOC: Generally refers to the diffuse release of vaporized hydrocarbon or other organic compounds. Fugitive emissions originate from equipment leaks and from large and/or diffuse sources.

Ground: 1. The electrical neutral line having the same potential as the surrounding earth. 2. The negative side of dc power supply. 3. Reference point for an electrical system.

Interferences: Any substance or species causing a deviation of instrument output from the value that would result from the presence of only the pollutant of concern.

Leak: A measured VOC concentration of the action level or greater, determined at a specified distance from the fugitive emission source (usually 0 cm). The concentration value that defines a leak can vary, depending on the regulation and the industry. A value of 10,000 parts per million by volume (ppmv) is by far the most often used and was used in this manual unless otherwise noted.

No Detectable Emission: A local VOC concentration at the surface of a source that indicates that a VOC emission (leak) is not present. Because background VOC concentrations may exist and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on a meter reading of less than 5 percent of the leak definition concentration indicates that a VOC emission is not present.

Precision: The degree of variation between repeated measurements of the same concentration.

Principle of Operation: The technique used to detect and measure the pollutant or parameter.

Process Stream: Process fluids such as reactants, intermediate products, final products, and by-products, that are contained within pipes, pumps, valves, etc., in a process unit. Steam, water, air, and other utility lines are not considered to be process streams.

Process Unit: Equipment assembled to produce an organic chemical as an intermediate or final product. A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient storage facilities for the final product.

Range: The lower and upper detectable limits. (The lower limit is usually reported as 0.0 ppm. This is somewhat misleading and should be reported as the true lower detectable limit.)

Repair: Adjustment or alteration of leaking equipment that reduces the screening value from greater than or equal to the action level (i.e., $\geq$10,000 ppmv) to below the action level (i.e., <10,000 ppmv).

Response Factor: A correction factor that quantifies the difference in meter response that a portable VOC analyzer has for various hydrocarbons and substituted organic chemicals.

Response Time: The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent (unless otherwise specified) of the ultimate recorded output. This measurement is the same as the sum of lag time and rise time.

Screening: The act of measuring the hydrocarbon concentration of a source with a portable hydrocarbon detector.

Screening Value: The hydrocarbon concentration (in ppmv) detected at a source with a portable hydrocarbon detector while traversing with the instrument probe around all the potential leak points of the source.

Source Type: Process unit equipment components that may emit fugitive emissions. Common source types of fugitive emissions are valves, pump seals, flanges, compressor seals, and sampling lines.

Thermocouple: The junction of two dissimilar metals which has a voltage output proportional to the difference in temperature between the hot junction and the lead wires (cold junction).

Type of Service: The physical state (gas, liquid, or both) of the material(s) contained in a specific pipeline or vessel. The terms liquid and gas are defined at operating condition of the process. Liquid process streams can be further subdivided into:

- Light VOC liquid--any process stream with a vapor pressure of equal to or greater than 0.3 kPa at 20°C (lighter than kerosene).
- Heavy VOC liquid--any process stream with a vapor pressure less than 0.3 kPa at 20°C.

Volatile Organic Compound (VOC): Any organic compound that participates in atmospheric photochemical reactions.

Warmup Time: The elapsed time necessary after startup for the instrument to meet stated performance specifications when the instrument has been shut down for at least 24 hours.

EPA-450/3-88-010

Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

October 1988

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GLOSSARY

Censored source - a source whose screening value is known to be above 100,000 ppmv but whose actual screening value is unknown.

Emission factor - the per component mass emission rate applicable to populations of sources, not individual component measurements.

Inaccessible source - a component which cannot be reached because it is beyond the reach of a 6-foot ladder.

Leak definition - monitoring instrument reading selected as the trigger value for initiating some action such as maintenance; e.g., 10,000 ppmv is the leak definition used by EPA.

Leak frequency - the percentage of sources (a particular equipment type and service) determined to be leaking based upon a chosen leak definition.

Leak rate - see mass emissions rate.

Leaking emission factor - the per component mass emission rate associated with the population of sources with screening concentrations at or above the leak definition.

Leaking source - a source whose screening concentration is greater than or equal to 10,000 ppmv.

Mass emissions rate - the quantity of volatile organic compound(s) released to the atmosphere in terms of total mass per unit time.

Monitoring instrument - portable hydrocarbon analyzer meeting the performance specifications given in Method 21.

Non-leaking emission factor - the per component mass emission rate associated with the population of sources with screening concentrations less than the leak definition.

Non-emitting source - a source whose screening value is 0 ppmv; a zero emission rate is assumed.

Non-leaking, emitting source - a source whose screening concentration is greater than 0 ppmv but less than 10,000 ppmv.

Screening value - raw monitoring instrument reading.

Screening concentration - the screening value (raw instrument reading) corrected by the appropriate response factor.

Unsafe-to-monitor equipment - equipment that exposes monitoring personnel to an immediate danger while screening the equipment.

EF = average emission rate per source

EF_1 = average emission rate per leaking source

EF_2 = average emission rate per non-leaking emitting source

X_{1i} = measured emission rate for the ith leaking source

X_{2i} = measured emission rate for the ith non-leaking emitting source

$\bar{X}_2$ = average measured emission rate for non-leaking emitting sources

N_1 = number of leaking sources

N_2 = number of non-leaking emitting sources

N_3 = number of non-emitting sources

N = total number of sources (including inaccessible sources)

n_1 = number of bagged leaking sources

n_2 = number of bagged non-leaking emitting sources

s_2^2 = estimate of the variance of the emission rates of the non-leaking emitting sources

$$= \sum_{i=1}^{n_2} (X_{2i} - \bar{X}_2)^2/(n_2 - 1)$$

y_{1i} = measured emission rate for the ith leaking source

y_{2i} = measured emission rate for the ith non-leaking emitting source

y_{1ai} = predicted emission rate for the ith leaking source screened <100,000 ppmv

y_{1bi} = measured emission rate for ith censored source

$\bar{y}_1$ = average predicted emission rate for leaking sources

$\bar{y}_2$ = average predicted emission rate for non-leaking emitting sources

$\bar{y}_{1a}$ = average predicted emission rate for leaking sources screened <100,000 ppmv

$\bar{y}_{1b}$ = average measured emission rate for censored sources

N_{1a} = number of leaking sources screened, <100,000 ppmv

N_{1b} = number of censored sources

n_{1b} = number of bagged censored sources

s_{y1}^2 = variance of the predicted emission rates of the leaking sources

$$= \sum_{i=1}^{N_1} (y_{1i} - \bar{y}_1)^2/(N_1 - 1)$$

s_{y2}^2 = variance of the predicted emission rates of the leaking sources screening <100,000 ppmv

$$= \sum_{i=1}^{N_2} (y_{2i} - \bar{y}_2)^2/(N_2 - 1)$$

s_{y1a}^2 = variance of the predicted emission rates of the leaking sources screening <100,000 ppmv

$$= \sum_{i=1}^{N_{1a}} (y_{1ai} - \bar{y}_{1a})^2/(N_{ia} - 1)$$

s_{y1b}^2 = variance of the measured emission rates of the censored sources

$$= \sum_{i=1}^{n_{1b}} (y_{1bi} - \bar{y}_{1b})^2/(n_{ib} - 1)$$

The symbol t is the value of the normal deviate corresponding to the desired confidence probability. If the number of bagged sources, n, is greater than or equal to 50 then the value of t approaches 1.96. If the sample size is less than 50, the percentage points may be taken from Student's t table with (n-1) degrees of freedom. The t distribution holds exactly only if the emission rates are normally distributed. Moderate departures from normality do not affect it greatly.

FOREWORD

The EPA's protocol for estimating equipment leak emissions is the result of detailed information gathering and data analysis. The protocol was written to provide a thorough understanding of acceptable approaches to generating process unit-specific emission estimates. In preparing this document, EPA has encouraged industry experts and trade association representatives to comment on the document's content. Chief among these contributors has been the Chemical Manufacturers Association (CMA), who has written a guidance document similar to this EPA protocol.

The CMA document is consistent with this guide. Both documents present acceptable approaches to generating emission estimates. Minor differences that exist between the two documents should not affect the acceptability of the emission estimates, provided the approaches to generating acceptable emission estimates are thoroughly understood. The CMA protocol includes a provision for the addition of bagging data from a single process unit to the EPA correlation curves to modify the leak rate/screening value correlation. While the EPA agrees with the technical premise that additional data could be added to the existing database, the Agency believes that, for practical reasons, this approach could create interpretation problems for control agencies. Therefore, the Agency does not support this approach. Currently, EPA is working with CMA to expand the existing database of equipment screening and bagging data. Ultimately, the Agency will consider the addition of the data currently being collected to the existing database. This effort may provide a better understanding of the magnitude of equipment leaks and appropriate controls for them. The EPA will consider appropriate modifications to this protocol when additional data collected during this interim period are analyzed.

1.0 INTRODUCTION

The purpose of this document is to present standard protocols for estimating mass emissions from equipment leaks. The EPA's interest in developing standard protocols is to assist states and industry in their efforts to estimate equipment leak emissions. Emission estimates are being developed for a variety of purposes, including permitting, inventories, and for the Superfund Amendments and Reauthorization Act (SARA).

The EPA previously developed equipment leak emission factors in previous work supporting standards. These factors represented emissions from typical facilities and were used to develop industry-wide emission estimates. The EPA's standards-setting process will continue to rely upon the average emission factors for industry-wide estimates. However, those estimates do not yield the accuracy that facilities are looking for today; therefore, there is now a need for more accurate emission estimating techniques.

Recognizing that the significance of our protocols is in providing a consistent approach to data collection and emissions estimates, EPA believes there is need for certain minimal requirements in any protocol. Our desire is to develop standard protocols for general use in generating unit-specific emission estimates for permitting and inventories.

This document describes methodologies the EPA considers appropriate for development of unit specific emission estimates for equipment leaks of organic compounds: volatile organic compounds (VOC) and volatile hazardous air pollutants (VHAP). Estimates generated using this protocol would be specific only to process units (or groups of sources) for which an estimate was made. EPA has made provision for extending such estimates beyond the limits of that group of sources.

Five methods for estimating emissions from equipment leaks from a specific chemical processing unit are included in the protocol:

- Average emission factor method;
- Leak/no-leak emission factor method;
- Three-strata emission factor method;
- Application of EPA correlations; and
- Development of new correlations.

They range from simply applying accurate equipment counts to the EPA's average emission factors to the more complex project of developing unit-specific correlations of mass emission rates and screening values.

All methods start with obtaining an accurate identification and count of equipment to be included in the emission estimate. The equipment counts can simply be used with the EPA's previously developed emission factors. The next step in complexity and refinement is the use of a portable organic analyzer to find the number of leaking and nonleaking sources. Leaking and nonleaking emission factors previously developed by the EPA can then be applied to generate the emission estimate.

A final refinement in a method employing discrete emission factors is that of applying emission factors to represent three different ranges of screening values. This has been called the stratified emission factor approach, or the three-strata approach. Applying the stratified emission factors requires more rigorous measurement of organic vapor concentrations with a portable instrument because actual concentration readings must be recorded instead of noting whether a piece of equipment is classified as leaking or not leaking.

The remaining two methods make use of correlation equations relating mass emissions to organic concentrations measured with a portable organic analyzer. The EPA's previously developed correlations are offered for use, and finally, if a process unit's emissions are statistically different from those represented by the EPA's correlations, provision is made for development of correlations specifically for that process unit.

Guidance and recommendations are offered for statistical analyses and for gathering the data required to execute the methods. The information is provided in the following major sections of this protocol:

- Section 2.0 Emission Estimate Development;
- Section 3.0 Source Screening;
- Section 4.0 Mass Emissions Sampling.

Section 2.0 details the types of data needed for making emissions estimates and how that data is to be applied. Sections 3.0 and 4.0 offer more detail on collection of data using a portable organic analyzer and using a technique known as "bagging," in which an enclosure is made around a potential leak point and emissions are actually measured. Additional reference material is included in the Appendices.

2.0 DEVELOPMENT OF EMISSION ESTIMATES

2.1 INTRODUCTION

In this section, five methods for estimating VOC and VHAP emissions from equipment leaks in chemical processing units are described. The methods increase in complexity and in the amount of data collection and analysis required. However, all five methods require some data collection, data analysis, and/or statistical evaluation. The five estimation methods and the options available for collecting and analyzing the data are shown in Figure 2-1. As the flow chart shows, the methods increase in rigorousness and complexity. The first method, the average factor method, is the least complex and demanding and the last method, developing site specific correlations, is the most complex and demanding. The end product of each of the procedures described is an emissions inventory for equipment leaks by type of equipment and by service (i.e., light liquid, gas, heavy liquid).

2.2 USE OF THE EPA'S AVERAGE EMISSION FACTORS

All of the methods require an accurate count of equipment components by type of equipment and by service. The most basic approach for estimating emissions merely requires application of average emissions factors developed by EPA to the equipment counts for the unit. EPA's average emission factors are shown in Table 2-1. The product of the emission factor and the number of equipment components yields the emission rate per source type, and the emission rates for all source types are summed to generate the unit-specific emission estimates.

The method EPA used for development of emission factors for individual equipment leak emission sources was described in reports on the Petroleum Refinery Assessment Study.[10,11] In this study, "screening" data were gathered using a portable organic vapor analyzer, and mass emissions were measured by enclosing individual pieces of equipment with bags or tents and measuring the organic material emitted.

These data permitted the development of leak rate/screening value correlations and emission factors for sources in petroleum refineries. Subsequently, EPA coordinated the SOCMI 24-unit Study,[15] a study of 24 individual chemical process units representing a cross-section of the SOCMI

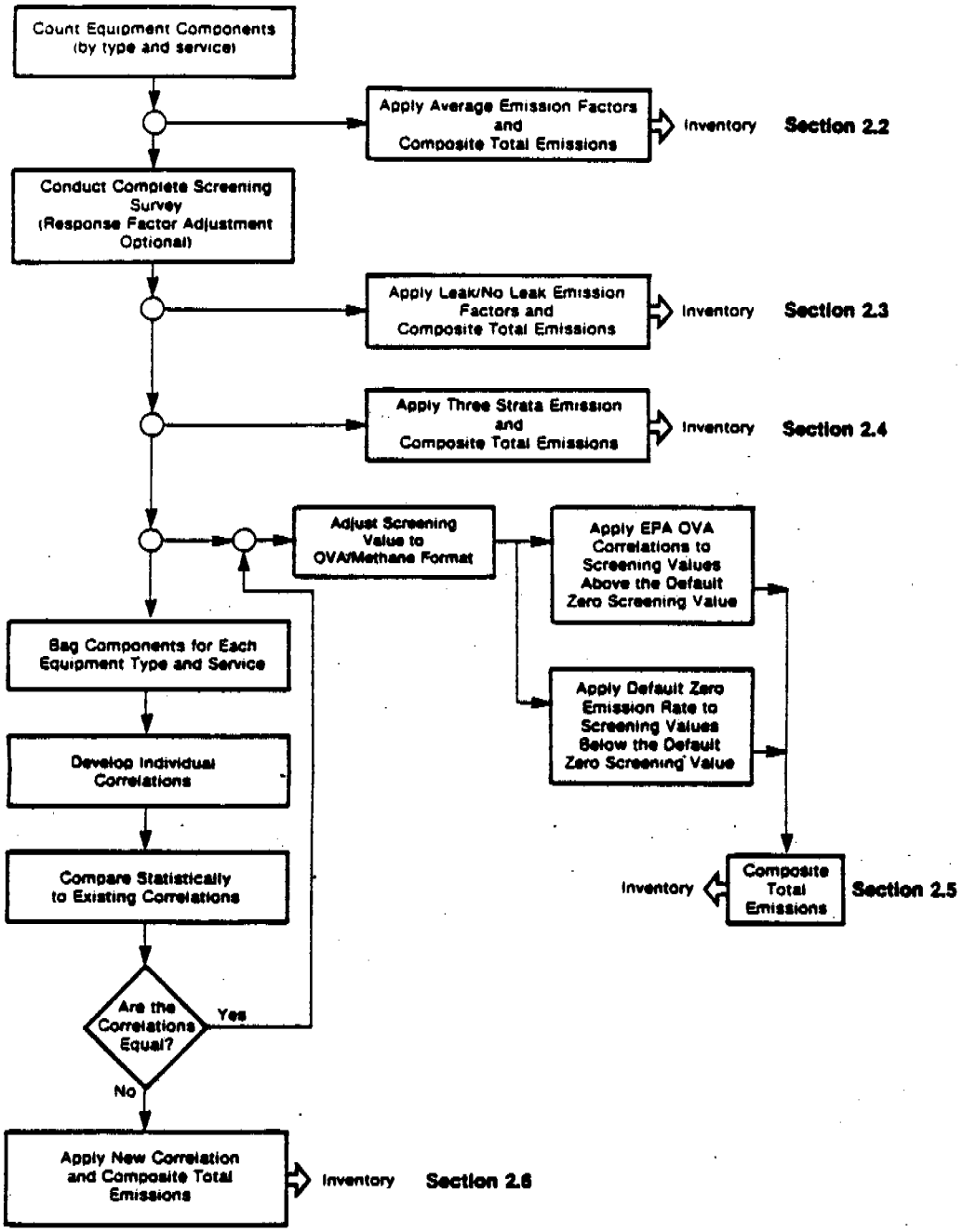


Figure 2-1. Strategy for Estimating Emissions from Equipment Leaks

TABLE 2-1. AVERAGE EMISSION FACTORS FOR FUGITIVE EMISSIONS

Equipment	Service	Emission Factor (kg/hr/source)
Valves	Gas	0.0056
	Light Liquid	0.0071
	Heavy Liquid	0.00023
Pump Seals	Light Liquid	0.0494
	Heavy Liquid	0.0214
Compressor Seals	Gas/Vapor	0.228
Pressure Relief Seals	Gas/Vapor	0.104
Flanges	All	0.00083
Open-Ended Lines	All	0.0017
Sampling Connections	All	0.0150

population, and a six-unit Maintenance Study.[14] As a result of these chemical process unit studies, leak rate/screening value correlations and emission factors were generated for valves in gas/vapor service in SOCMI. Leak rate/screening value correlations were also generated for light liquid valves and light liquid pumps in SOCMI, but industry average emission factors were not developed.

2.3 THE LEAK/NO-LEAK APPROACH

The second method offers some refinement over the average emission factor method, thereby allowing some adjustment to individual unit conditions and operation. This method and all the remaining methods require screening of all equipment to be included in the inventory using a portable analyzer. Equipment that is dangerous to screen may be omitted from the set of equipment components to be screened. Their emission rates may be estimated using the EPA's average factors presented in Table 2-1.

Insulated equipment can be considered difficult-to-monitor equipment. The decision to remove insulation to facilitate screening is left to individual judgement. If insulation is not removed, the insulated component is assumed to leak at the same rate as a similar uninsulated component.

For flanges, a reduced number of components may be screened. Appendix E describes how to select the sample size for flanges. In compiling screening values for use in this technique (or any of those that follow), a response factor may be applied to correlate the screening values measured for the chemical in the line to the screening values observed in calibrating the instrument to another chemical. For a discussion of response factor adjustment, see Section 3.2.2.1.

The leak/no-leak approach to estimating emissions is based on the assumption of only two emission rates and two populations of equipment components: sources that "leak" (with screening concentrations greater than or equal to 10,000 ppmv) and sources that do not "leak" (with screening concentrations less than 10,000 ppmv).

The basis of this approach is as follows: when a group of sources leak, they leak at a certain emission rate on the average. Similarly, as a group, non-leaking sources have, on the average, a certain mass emission rate

associated with them. Thus, the overall emission estimate for a population of emission sources consists of two components: leaking source emissions and non-leaking source emissions.

Table 2-2 presents leaking and non-leaking emission factors previously determined by EPA for equipment leaks. EPA generated leaking and non-leaking emission factors using: 1) emission factors generated from empirical screening distribution data and leak rate/screening value correlations, 2) the leak frequencies associated with the emission factors, and 3) the percent of mass emissions associated with the leaking sources. The detailed procedure for generating leaking and non-leaking emission factors has been previously published in the "Additional Information Document" (AID)[13] for fugitive emission sources of organic compounds and is also described in a document entitled "Emission Factors for Equipment Leaks of VOC and HAP."[16]

The application of the leak/no-leak approach for estimating emissions is shown in the following example for a hypothetical chemical process unit.

Table 2-3 presents the data for this hypothetical process unit needed to apply the leak/no-leak procedure for estimating emissions. The first column shows the number of sources in the process unit by source type. The second column shows the number of sources with screening values greater than or equal to 10,000 ppmv (i.e., leaking sources). The percentage of sources leaking is shown in the third column. The emission estimates for this hypothetical process unit can then be computed using the leaking and non-leaking emission factors in Table 2-2. For example, three of the 47 pump seals in light liquid service were found to be leaking. Using the leak/no-leak approach, the emission estimate is generated:

(0.437 kg/hr/source)(3) + (0.012 kg/hr/source)(47-3),

or 1.84 kg/hr. The emission estimate per source for pumps in light liquid service could then be computed by dividing the unit-specific emission estimate by the equipment count. The last column in Table 2-3 shows the annual emission estimates by source type for the hypothetical unit.

While this example illustrates how total VOC emissions per source type are calculated, a similar procedure can be used to estimate emissions for a particular species in the line. For example, consider this same hypothetical case where the light liquid pumped contained 20 weight percent of Compound A.

TABLE 2-2. LEAKING AND NON-LEAKING EMISSION FACTORS FOR FUGITIVE EMISSIONS (kg/hr source)

Equipment	Service	Leaking (≥10,000 ppm) Emission Factor	Non-leaking (<10,000 ppm) Emission Factor
Valves	Gas[a]	0.0451	0.00048
	LL[b]	0.0852	0.00171
	HL[c]	0.00023[d]	0.00023
Pump Seals	LL	0.437	0.0120
	HL	0.3885	0.0135
Compressor Seals[e]	Gas	1.608	0.0894
Pressure Relief Valves	Gas	1.691	0.0447
Flanges	All	0.0375	0.00006
Open-Ended Lines	All	0.01195	0.00150

[a]The leaking and non-leaking emission factors for valves in gas/vapor service are based upon the emission factors determined for gas valves in ethylene, cumene, and vinyl acetate units during the SOCMI Maintenance Study. References 8 and 15.

[b]LL - light liquid service.

[c]HL - heavy liquid service.

[d]Leaking emission factor assumed equal to non-leaking emission factor since the computed leaking emission factor (0.00005 kg/hr/source) was less than non-leaking emission factor.

[e]Emission factor reflects existing control level of 60 percent found in the industry; control is through the use of barrier fluid/degassing reservoir/vent-to-flare or other seal leakage capture system.

TABLE 2-3. ESTIMATE OF "UNCONTROLLED" FUGITIVE EMISSIONS FOR A HYPOTHETICAL CASE

Source	Number Screened	Number Leaking	Percent Leaking	Computed Emission Estimate[a] (per Source) kg/hr/source	Annual[b] Emissions Mg/yr
Pump Seals					
Light Liquid	47	3	6.4	0.0391	16.1
Heavy Liquid	3	1	33.3	0.1385	3.6
Valves					
Gas/Vapor	625	19	3.0	0.0018	10.1
Light Liquid	1180	13	1.1	0.0026	27.2
Heavy Liquid	64	0	0	0.00023	0.1
Pressure Relief Valves					
Gas/Vapor	31	1	3.2	0.0978	26.6
Open-Ended Lines	278	9	3.2	0.0018	4.5
Compressor Seals	4	0	0	0.0894	3.1
Sampling Connections	70	-	-	0.0150	9.2
Flanges	2880	20	0.7	0.00032	8.1

[a]Based on values from Table 2-2, using EE = [LEF * PCL + NLEF * (100-PCL)]/100 where

EE = Emission Estimate (per Source)
LEF = Leaking Emission Factor
NLEF = Non-leaking Emission Factor
PCL = Percent of sources found leaking

[b]This hypothetical process unit is assumed to be in continuous operation, so it operates for 8,760 hours per year. Batch or campaign processes may operate fewer hours per year, so the annual emissions would be prorated to account for the hours the equipment contained the chemical.

The emission estimate for Compound A for light liquid pumps is computed by applying the weight percent (20 percent in this case) to the emission estimate generated above:

(0.20)(1.84 kg/hr) = 0.368 kg/hr.

As another example, consider the hypothetical case where the light liquid pumped contained only 80 weight percent VOC and Compound A accounted for 20 percent by weight. The emission estimate for Compound A for light liquid pumps is computed as:

(0.2/0.8)(1.84 kg/hr) = 0.460 kg/hr

In other words, compound A accounts for one-fourth of the total VOC emissions of 1.84 kg/hr. As before, emissions per source can be determined by dividing the estimate by the number of components involved. Emission factor estimates calculated in this manner may then be applied to the equipment counts (where the material in the process line contained 20 weight percent of compound A) to estimate emissions of compound A for that specific process unit.

2.4 APPLICATION OF STRATIFIED EMISSION FACTORS

Another approach to generating emission estimates involves a refinement of the leak/no-leak approach discussed above. The leak/no-leak approach is based on two emission rates and two populations (i.e., leaking and non-leaking sources). The stratified emission factor approach, on the other hand, is based on several population and emission factors spanning several discrete screening value ranges.

Screening values in the EPA SOCMI data base are distributed widely from 0 ppmv to over 100,000 ppmv. The mass emissions are correspondingly distributed. The stratified emission factor approach for estimating emissions segments this distribution into discrete intervals to account for different ranges of screening values. The following ranges are used:

- 0 - 1,000 ppmv;
- 1,001 - 10,000 ppmv; and
- over 10,000 ppmv.

Using data gathered during previous EPA studies, emission factors for each screening value range have been generated. These stratified emission factors represent the leak rates measured during fugitive emissions testing.

Their development incorporated the statistical methods used by the EPA in developing other emission factors. The emission factor for each discrete interval is presented in Table 2-4 by equipment type and service.

This method requires that screening of all equipment (except that which is hazardous to screen) be conducted in accordance with methods described in Section 3 of this report. All screening values must be recorded according to the applicable ranges. Then, as with the leak/no-leak approach, the total emission estimate is generated by applying the number of components in each screening value range to the appropriate emission factor and summing each subtotal. An example of this procedure, shown in Table 2-5, illustrates how to implement the stratified emission factor approach.

2.5 LEAK RATE/SCREENING VALUE CORRELATIONS

Mathematical correlations offer an additional refinement to estimating emissions from equipment leaks by providing a continuous function over the entire range of screening values instead of discrete intervals. The EPA has published correlations relating screening values to mass emissions rates. As shown in Appendix D, there are four correlations which can be applied to all equipment types and services. The EPA's correlations are based upon OVA measurements taken using Method 21. The instrument was calibrated to methane (see Method 21). Screening value measurements used with these published correlations should be in this same format. For example, if a TLV instrument calibrated to hexane were used to gather screening data, the data must be transformed to represent measurements gathered using an OVA, calibrated to methane, before using the published correlations. If a detector fails to meet Method 21 specifications or published transformations are not available, an instrument response curve must be developed to relate screening values to actual concentrations in the appropriate format (OVA/methane). Development of this screening value correction curve should be done in the laboratory before the detector is used in the field.

Another correction factor that can be applied to Method 21 and non-Method 21 instruments is the response factor. For many compounds, the instrument response is non-linear with increasing screening value. In terms of the basic leak/no-leak approach described in a previous section, a single

TABLE 2-4. STRATIFIED EMISSION FACTORS FOR EQUIPMENT LEAKS
(kg/hr/source)

Source	Service	Emission Factors (kg/hr/source) for Screening Value Ranges, ppmv		
		0-1,000	1,001-10,000	Over 10,000
Compressor seals	Gas/vapor	0.01132	0.264	1.608
Pump seals	Light liquid	0.00198	0.0335	0.437
	Heavy liquid	0.00380	0.0926	0.3885
Valves	Gas/vapor	0.00014	0.00165	0.0451
	Light liquid	0.00028	0.00963	0.0852
	Heavy liquid	0.00023	0.00023	0.00023
Flanges, connections	All	0.00002	0.00875	0.0375
Pressure relief devices	Gas/vapor	0.0114	0.279	1.691
Open-ended lines	All	0.00013	0.00876	0.01195

TABLE 2-5. ESTIMATE OF FUGITIVE EMISSIONS USING STRATIFIED EMISSION FACTORS FOR A HYPOTHETICAL CASE

Source	Number Screened	Number of Sources Screening (ppmv)			Computed Emission Estimate	
		0-1,000	1,001-10,000	Over 10,000	per Source Type[a] (Kg/hr)	per Source[b] (Kg/hr/source)
Compressor seals						
Gas/vapor	4	3	1	0	0.298	0.0745
Pump seals						
Light liquid	47	32	12	3	1.776	0.0378
Heavy liquid	3	1	1	1	0.485	0.1616
Valves						
Light liquid	1,180	1,020	147	13	2.81	0.00238
Heavy liquid	64	63	1	0	0.01472	0.00023
Flanges	2,880	2,600	160	20	2.20	0.00076
Pressure relief devices						
Gas/vapor	31	25	5	1	3.37	0.1087
Open-ended lines	278	236	33	9	0.427	0.00154

[a]Based on emission factors from Table 2-2, where $EE = (NL_1 * SEF_1) + (NL_2 * SEF_2) + \ldots$

EE = Emission Estimate

NL_1, NL_2, etc. = Number leaking in 1st range (0-1,000), Number leaking in 2nd range (1,001-10,000), etc.

SEF_1, SEF_2, etc. = Stratified emission factor for 1st range, stratified emission factor for 2nd range, etc.

[b]Computed Emission Estimate per source = Computed Emission Estimate per Source Type/Number Screened.

point response factor adjustment at the leak definition of 10,000 ppm is adequate. If, however, the correlations are to be used, the best estimate of screening concentration over the entire range is needed. Therefore, a correction for non-linear response must be made. This can be accomplished in the laboratory by generating a response curve.

The flow chart in Figure 2-1 shows a separate treatment of "zero" screening values. The function describing the correlation of leak rate and screening value becomes discontinuous for zero and near zero values. The correlation function mathematically predicts zero emissions for zero readings on the portable instrument. Empirically speaking, however, the EPA's data shows this prediction to be incorrect. Mass emissions have been measured from equipment showing no screening concentration above zero. The reason for this involves the detector accuracy. In the Refinery Assessment Study mass emissions corresponding to a screening value of 200 ppm or less could not be quantified because the accuracy limit of the detector was 200 ppm. To handle this discontinuity at the low end of the correlation, the EPA has derived a "default zero" screening value (8 ppm) and an associated mass emission rate for the screening values between zero and that default zero reading. These "default zero" values and emission rates shown below were derived as shown in Appendix F from mass emissions data gathered in chemical plants and the published leak rate/screening value correlations shown in Appendix D:

Equipment Type/Service	"Default Zero" Screening Value, ppm	Zero Screening Value Emission Rate (kg/hr/source)
Valves, gas	8	0.000033
Valves, light liquid	8	0.000451
Flanges	8	0.000093
Pumps and all other components	8	0.000039

These emission factors should be applied to equipment components screening between 0 and 8 ppm. The published correlations would be applied to all screening concentrations above 8 ppm. The total emissions estimate for equipment leaks is generated by totaling emissions estimates for all "default zeroes" and adding that total to the total estimates generated using the correlations. Appendix G presents an alternative methodology for generating unit-specific default zero emission rates.

2.6 UNIT-SPECIFIC CORRELATIONS

A process unit may develop its own correlations if leak rates are statistically different from EPA's rates. The steps involved in generating a unit-specific emissions estimate using correlations developed specifically for that unit are:

1. Gathering of mass emission data and calculation of mass emission rate (leak rate);
2. Development of leak rate/screening value correlations;
3. Statistical consideration of leak rate/screening value correlations;
4. Application of leak rate/screening value correlation to the empirical screening data; and
5. Prediction of emissions.

These steps are discussed individually in the following sections.

2.6.1 Generation of Mass Emissions Data

After complete screening of the process unit is done for all source types (except possibly flanges), selected sources can be bagged to measure the mass emission rate. The sources selected for mass emission measurement should be rescreened at the time of bagging. The mass emission rate determined by bagging and the rescreening value can then be used to validate the application of EPA's correlations to the process unit. Alternatively, the measurements can be used in development of leak rate/screening value relationships for that specific unit. The screening value can be affected by the portable screening instrument used and the gas used to calibrate the instrument. The EPA leak rate/screening value correlations are based on data gathered using an OVA instrument calibrated with methane.

If other instruments or calibration gases are used, then the screening value should be adjusted (using theoretical or empirical correction factors) to be equivalent to values measured using an OVA calibrated with methane prior to any comparisons to the EPA equations. Instrument readings above the saturation point of the detector must be bagged to quantify the emission rate.

The amount of leak rate testing (bagging) that should be done depends on the objective of the data collection. If one wishes to check the fit of EPA published equations to a particular process unit, as few as four leak rate measurements of a particular source type in a particular service may be

adequate. If it is desirable to develop new equations, 30 leak rate measurements should be obtained. Because of the inherent variability of leak rate/screening data, it is difficult to detect differences between correlations with fewer than 30 data pairs. However, the statistical goal is to generate estimates that are within 50 percent of the mean value with 95 percent confidence. If this statistical goal can be achieved with fewer data pairs, then fewer data pairs are acceptable.

Consider a hypothetical process unit having a large population of sources with screening values well distributed over the range of 0 to 100,000+ ppmv. To develop statistically valid leak rate/screening value correlations, mass emissions data must be collected from individual sources that have screening values distributed over the entire range. For each source type (i.e., valves, pumps, etc.) and service (i.e., gas, light liquid, etc.), a random sample of six sources should be chosen for bagging from each of the following screening value ranges:

Screening Value Range (ppmv)
1 - 100
101 - 1,000
1,001 - 10,000
10,001 - 100,000
> 100,000

If the maximum response of the screening instrument is 100,000 ppmv, then 20 or all (whichever is less) of the sources screened at 100,000 ppmv should be bagged. If six sources are not available in a particular screening value range, additional sources from the nearest range should be tested. If screening values greater than 10,000 ppmv are not found in the process, the following five groups can be used:

1 - 100 ppmv
101 - 300 ppmv
301 - 1,000 ppmv
1,001 - 3,000 ppmv
3,001 - 10,000 ppmv

Similar groupings can be developed if all sources in the unit screen less than 1,000 ppmv.

If a statistical determination is made that estimates within 50 percent of the mean value with 95 percent confidence can be achieved with fewer than 30 data pairs, the following bagging strategies are recommended:

SCREENING VALUE RANGE (ppmv)	TOTAL NUMBER OF LEAK RATE MEASUREMENTS			
	4	8	12	20
1 - 100	2	2	3	4
101 - 1,000		1	2	4
1,001 - 10,000		1	2	4
10,001 - 100,000	2	2	3	4
> 100,000		2	2	4

These groupings and recommended number of sources are given as guidelines. They are based on experience in measuring leak rates and developing leak rate/screening value equations. Other source selection strategies can be used if an appropriate rationale is given.

2.6.2 Development of Leak Rate/Screening Value Correlations

With appropriate mass emission data and screening values, leak rate/screening value correlations can be generated. Least-squares regression analyses are done for each source type/service, regressing the logarithm of the nonmethane leak rate on the logarithm of the screening concentration, according to

$$\text{Log (leak rate)} = B_0 + B_1 \text{ Log (screening concentration)},$$

where

B_0, B_1 = model parameters.

All analyses should be done using logarithms of both the leak rate and screening concentration. Confidence intervals should be calculated for the estimated equation (Reference 19, pages 28-31). A scale bias correction factor (Reference 20) is required in transforming the equation in the log-scale back to the original units. A statistician should be consulted unless one is familiar with this type of analysis. Bagged sources whose screening values are known to be above 100,000 ppmv but whose actual screening

values are unknown should not be used to fit the regression line described above. For those sources censored at 100,000 ppmv and which were not bagged, leak rates should be estimated from the average leak rate for those censored sources that were bagged.

2.6.3 Statistical Considerations of Leak Rate/Screening Value Correlations

The predictive equations resulting from the least-squares regression analyses discussed above must be statistically evaluated.

If new correlation equations are developed, they must be shown to be statistically different from the existing correlations developed during the refinery and SOCMI studies. If the new correlations are statistically different from the existing correlations, the new correlations may be used in the development of the unit-specific emission estimates for that specific class of sources. If not, the EPA's correlations should be used. The correlations can be compared graphically or mathematically.

2.6.3.1 Graphical Comparison of EPA vs. Other Correlations. If enough data are collected to develop a process specific leak rate/screening equation, then this equation should be compared to the published EPA equation. The EPA's predictive equation should be used unless the equation developed for the specific process unit is found to give significantly different estimates. This comparison can be done graphically by drawing the process specific equation on a graph of the EPA equation. Figure 2-2 (from Reference 14, page 66) is an example of such a graph.

A graphical comparison may also be made by plotting the leak rate/screening data from the process on a log-scale plot of the EPA equations. The log scale is preferred so that linear comparisons can be made. Figures 2-3 through 2-5 (from Reference 14, pages 57-62) show such plots of the EPA equations. The leak rate/screening value measurements used to develop the equations are also shown on the plots. These plots were developed from draft versions of the correlations. The correlations were refined when censored sources were included in modeling the leak rate/screening value relationships. Only small differences exist between the old and new models (see Reference 8, pages 14-18).

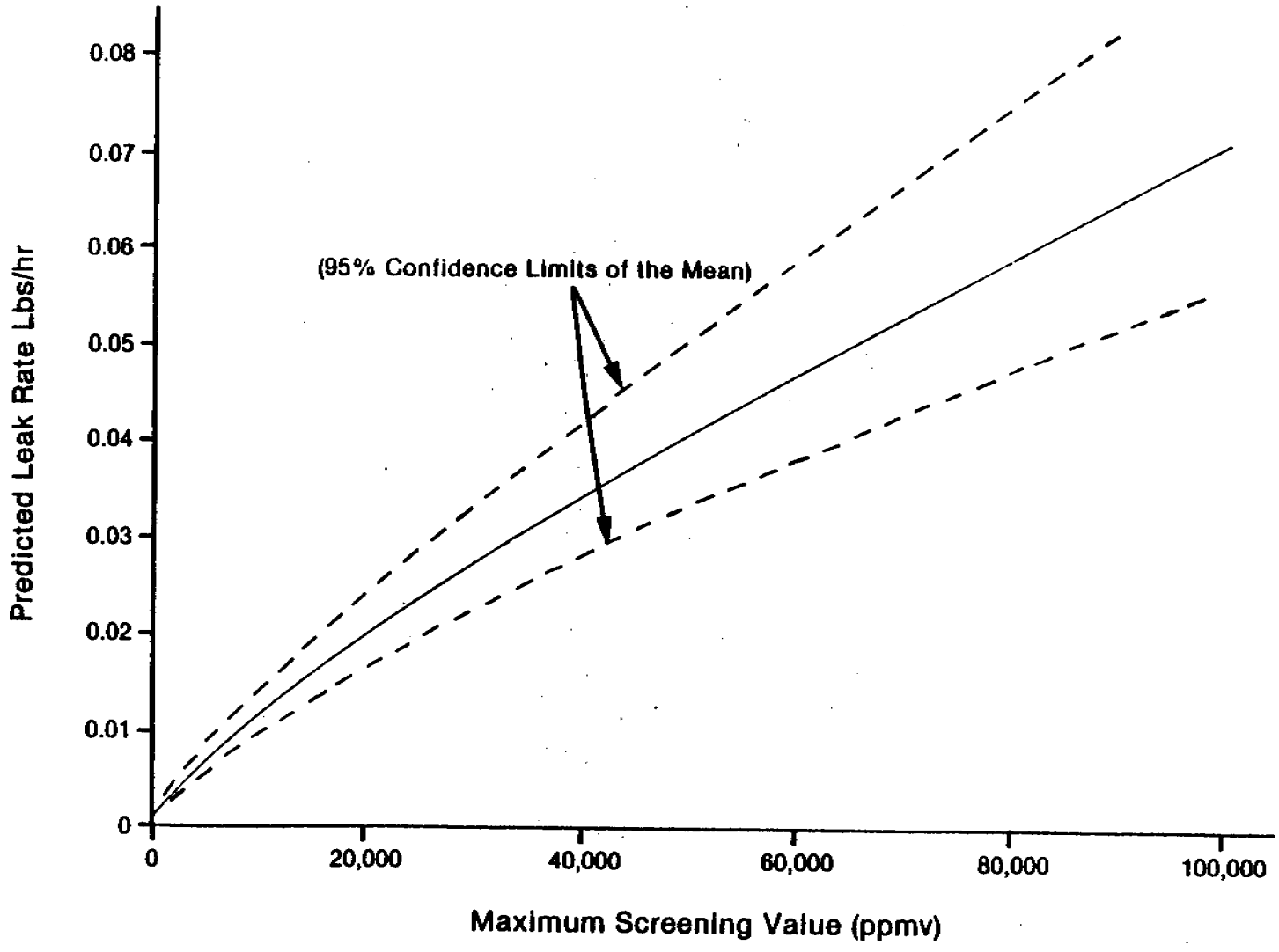


Figure 2-2. Modeled relationship - leak rate vs. OVA for valves in gas service.

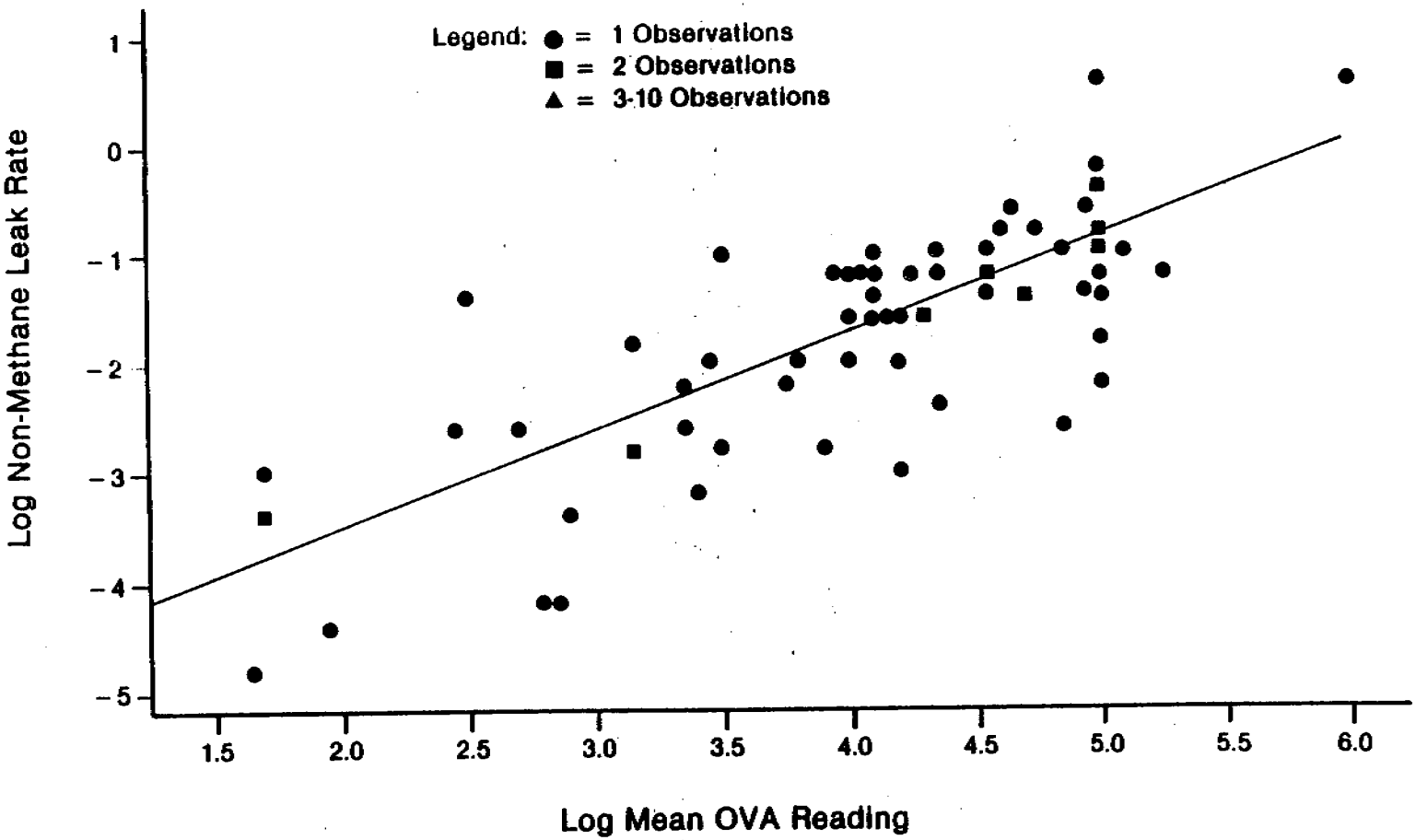


Figure 2-3. Log_{10} leak rate vs. log_{10} OVA reading for pump seals.

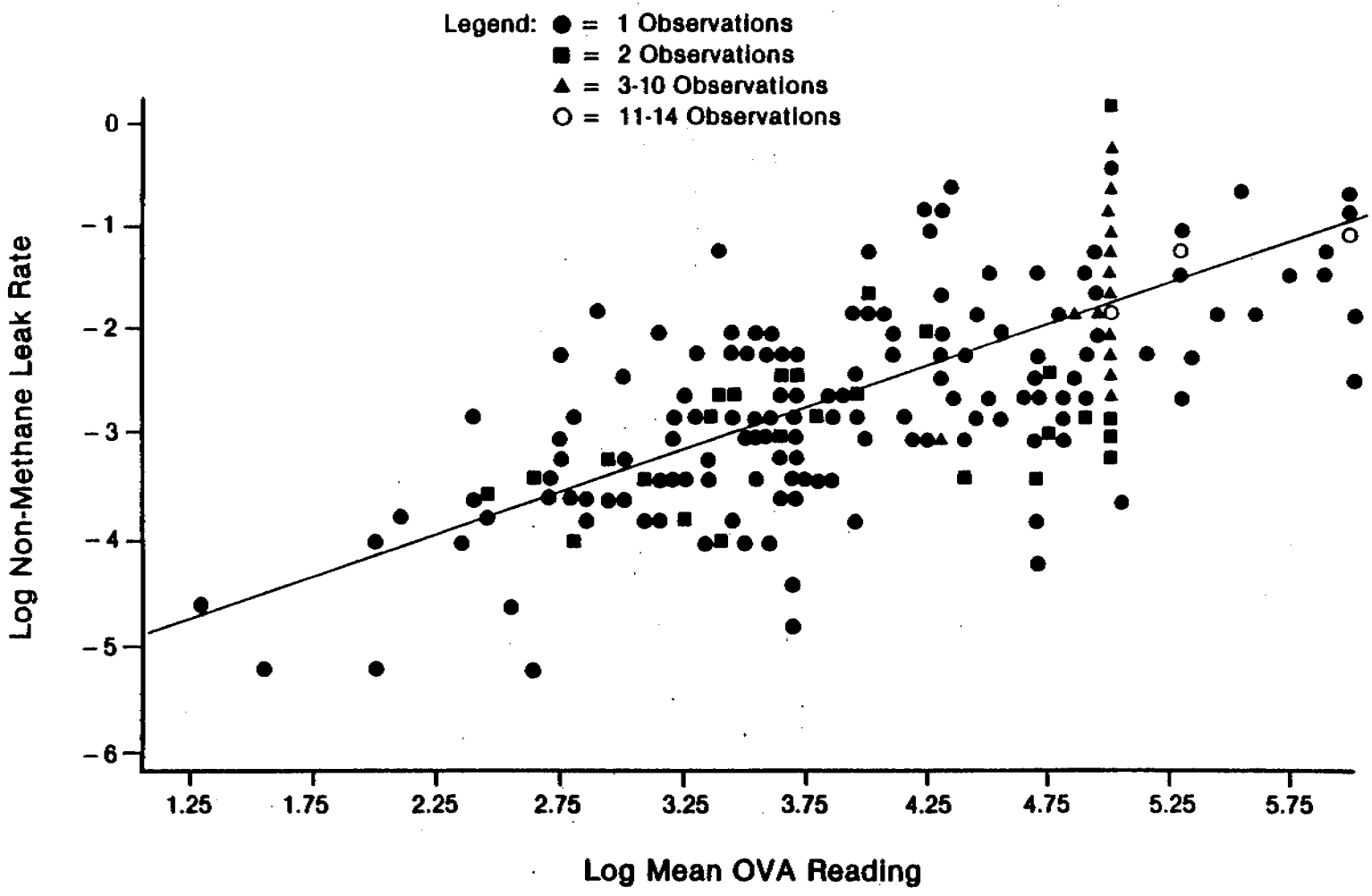


Figure 2-4. Log_{10} leak rate vs. log_{10} OVA reading for valves in gas service.

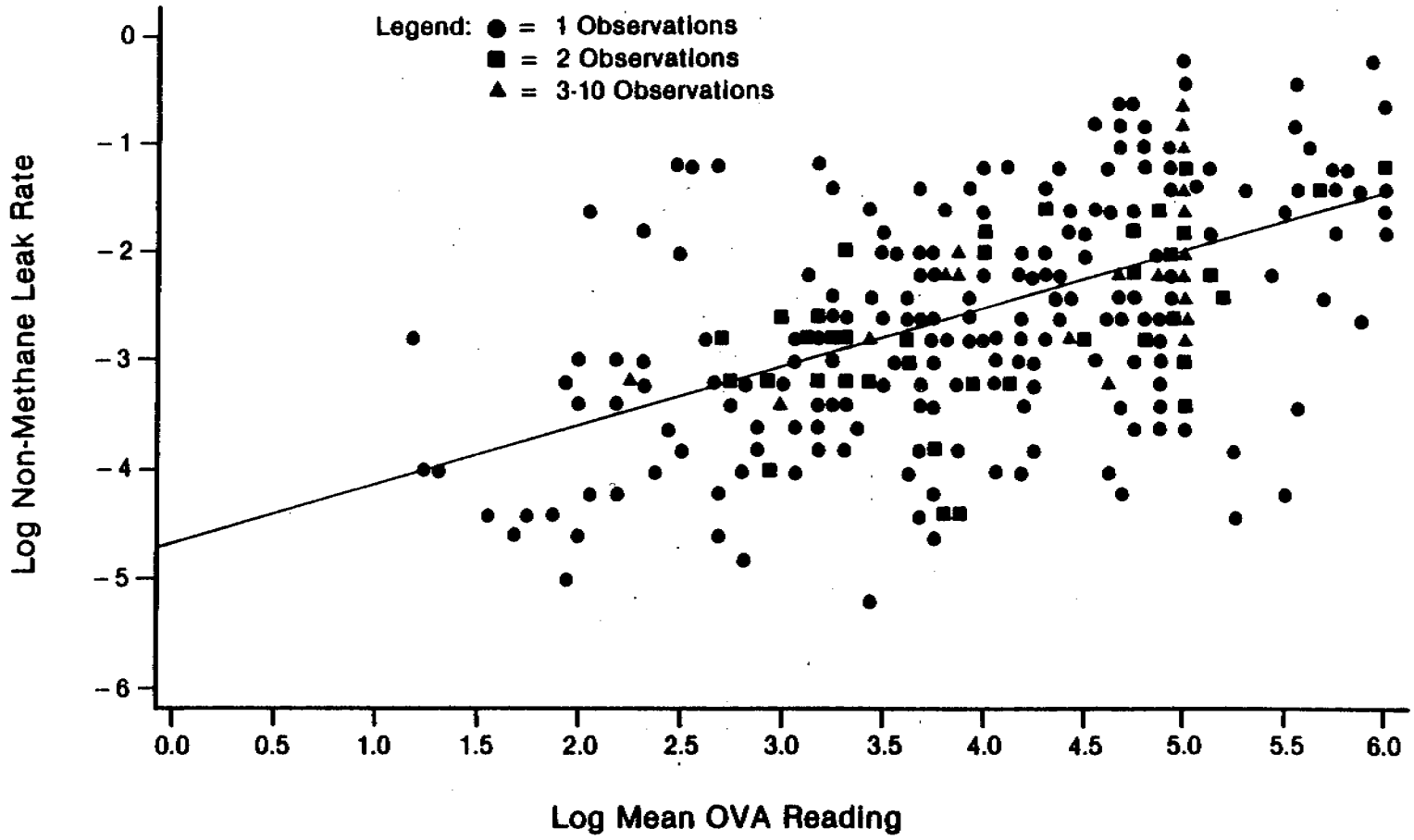


Figure 2-5. Log_{10} leak rate vs. log_{10} OVA reading for valves in liquid service.

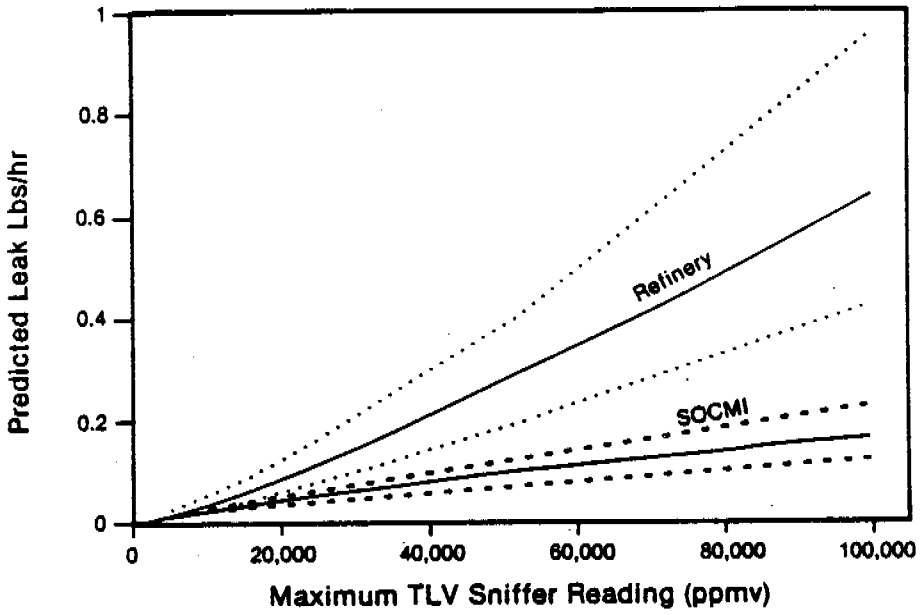
If the points fall on both sides of the line representing the equation and are within the range of data points used to develop equations, then it is reasonable to use the published equations for estimating emissions from the process. Statistical tests, such as the Wilcoxon Paired Replicate Rank test (Reference 21, pages 401-403) can be used to aid in the decision of reasonableness of the equations.

As an example, Figure 2-6 (from Reference 14, page 79) shows two comparisons of equations developed by EPA from Petroleum Refineries to the SOCMI equations. The first comparison (valves in gas service) shows the refinery equation consistently estimates greater leak rates throughout the curve. The confidence limits for the two equations do not overlap. For this comparison, it is obvious that different equations are required for the two different types of process units.

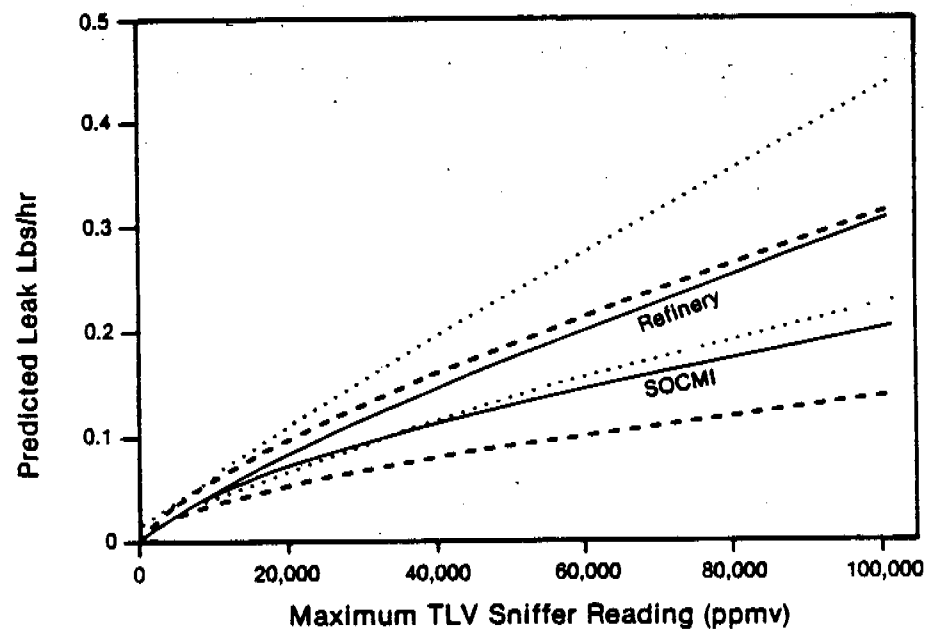
A second example of graphical comparison is shown in Figure 2-6 for valves in light-liquid service. In this case the refinery equation estimates greater leak rates than the SOCMI equation, but the refinery equation is within the confidence bands for the SOCMI equation. The SOCMI equation falls below the lower confidence band for the refinery equation for valves screening greater than 30,000 ppmv. The comparison is not as clear as the valves in gas service. Since there were about 300 data pairs used to develop the SOCMI equation, it should be used to develop estimates for SOCMI units.

For comparisons of process specific equations to the EPA equations there will usually be fewer data sets used to develop the specific equations. This will result in much wider confidence bands for the process specific equations. If 30 pairs of data are selected, the upper confidence band should be less than a factor of two greater than the upper confidence band predicted by the equation.

The form of the graph can be modified to facilitate the comparison of the equations. If most of the sources screen less than 10,000 ppmv, the equations can be graphed on a scale from 0 to 10,000 ppmv. The equations can also be graphed on a log-scale to make the comparisons linear. However, the scale-bias correction factors would not be incorporated if the comparisons are made in this way. Therefore, this type of comparison is not recommended.



Valves-Gas



Valves-Light Liquid

Dotted lines are 90% confidence bounds for the "Refinery" model
Dashed lines are 95% confidence bounds for the SOCMI model

Figure 2-6. Comparison of SOCMI and refinery leak rate correlations.

2.6.3.2 Statistical Comparison of EPA vs. Other Correlations. A more formal approach to comparing leak rate/screening value equations is to use statistical tests to compare the parameters estimated by the equations. The important parameters of the leak rate/screening value equations (developed on a log-scale) are the following:

1) the intercept (Bo);
2) the slope (Bl);
3) the standard error (Se).

Statistical tests for the slope and intercept are also available (Reference 19, page 24-33).

Ninety-five percent confidence intervals for the slope and intercept were developed for each of the SOCMI leak rate/screening value equations (Reference 8, pages 24-25). For example, the slope of the equations for valves in gas service using the OVA was estimated to be 0.693. The 95 percent confidence interval for this slope is given as 0.53 to 0.85. If a slope estimated from a particular SOCMI process unit is within this confidence interval, then the EPA equation provides a reasonable slope for a predictive equation. If the slope estimate is outside the confidence interval for the EPA correlation, the confidence interval for the slope estimated by the unit-specific equation must be evaluated. Reference 19 indicates how to make these evaluations.

A statistical test to compare the standard errors for two equations can be done using an F-test (Reference 20, page 31 or Reference 21, pages 111-116). Since the standard error is the key component of the scale-bias correction factor, this comparison of standard errors will also serve as a comparison of the scale bias correction factors incorporated in the two correlations.

2.6.3.3 Other Statistical Analyses. There are other types of statistical analysis that can be used in the development, evaluation, and comparison of leak rate/screening value equations. A General Linear Models analysis of the leak/rate screening value data (Reference 20, Chapter 2) can be used to develop equations and to test for different leak rate/screening relationships for different groups of data. This approach was used in Reference 14 (pages 51-53) to evaluate differences between the cumene, ethylene, and vinyl acetate units.

2.6.4 Generation of Emission Estimates

The generation of the emission estimate using correlations developed for specific process units makes use of the empirical screening data and the leak rate/screening value correlations. The leak rate/screening value correlations are applied to the screening data to calculate predicted emission rates.

Emission rates are estimated for all emitting sources (including those sources which were bagged) by:

$$\text{Predicted emission rate} = \exp\left[B_0 + B_1 \log(\text{screening concentration})\right] \times (\text{scale bias correction factor})$$

B_0 and B_1 are the coefficient estimates either published by EPA (Appendix D) or developed from a linear regression analysis, if site specific correlations are used. The results presented in arithmetic scale are adjusted to represent mean emission rates using the scale bias correction factor.

The sum of the individual predicted leak rates represents the total mass emission estimate for a given type of source and service being considered. An emission estimate per source can be derived by averaging the total emission estimate over the number of sources in the distribution.

2.6.5 Statistical Considerations for the Predicted Emission Estimate

This section presents formulas for calculating the 95 percent confidence intervals for the predicted emission estimate. For clarity, formulas for calculating the emission estimate per source and total emission estimate are presented also. Definitions for the formulas are presented in the Glossary.

For the Average Emission Rate Per Leaking Source (EE_1):

$$EE_1 \text{ without censoring} = \frac{\sum_{i=1}^{N_1} Y_{1i}}{N_1},$$

with a 95 percent confidence interval of:

$$EE_1 \pm \frac{t s_{y1}}{(N_1)^{1/2}}$$

$$EE_1, \text{ with censoring} = \frac{N_{1a}\,Y_{1a} + N_{1b}Y_{1b}}{N_1},$$

with a 95 percent confidence interval of:

$$EE_1 \pm \frac{t}{N_1}\left([N_{1a}s_{y1a}]^2 + \frac{N_{1b}}{n_{1b}} - 1[N_{1b}s_{y1b}]^2\right)^{1/2}$$

For the Average Emission Rate Per Non-leaking Emitting source (EF_2):

$$EE_2 = \frac{\sum_{i=1}^{N_2} Y_{2i}}{N_2},$$

with a 95 percent confidence interval of:

$$EE_2 \pm \frac{ts_{y2}}{(N_2)^{1/2}}$$

For the Average Emission Rate Per Source (EE):

$$EE = \frac{N_1EE_1 + N_2EE_2}{N_1 + N_2 + N_3},$$

with 95 percent confidence intervals of:

$$EE \pm \frac{t}{N_1 + N_2 + N_3}\left([N_1s_{y1}]^2 + [N_2s_{y2}]^2\right)^{1/2} \text{ without censoring.}$$

Total Emissions + N x EE (use the EE confidence limits above multiplied by N).

3.0 SOURCE SCREENING

This section presents protocols and methodologies for conducting screening of equipment components with a portable organic analyzer. The overall survey procedure is presented to give the perspective of a unit-wide screening plan. In addition, screening protocols are given for the different equipment types. The selection of an appropriate portable monitoring instrument is discussed and a section on data handling is also included.

3.1 SCREENING SURVEY PROCEDURES

For development of a unit-specific emission estimate, the concentration of organic materials at seals, shafts, and other potential leak points must be measured. In preparing to screen all equipment in a unit, all equipment to be included in the emission estimate unit needs to be identified. A listing of equipment types that are potential sources of fugitive emissions is given in Table 3-1.

The first step in the screening survey is to define precisely the process unit boundaries. This is usually quite straightforward, but occasionally multiple units may be built on the same pad and share some common facilities. A process unit can be defined as the smallest set of process equipment which can operate independently and includes all operations necessary to achieve its process objective. The exact basis for the unit definition should be documented. A plot plan of the unit should be obtained and marked with the appropriate boundaries.

The next step is to obtain a simplified flow diagram of the process and note the process streams. The actual screening and data collection can be done most systematically by following each stream. For instance, a logical starting point would be where one of the feed lines enters the process boundary. The screening team would follow that line, screening all sources, until the line terminates at the flanges of a reactor or separation step. Screening would then continue on the outlet side of the reactor or separation equipment. Minor loops like a bypass around a control valve, pump, or heat exchanger should be screened on the initial pass. Larger loops of process equipment, such as parallel passes and processing alternatives, are more

TABLE 3-1. FUGITIVE EMISSION SOURCES

Equipment Types
Pump seals
Compressor seals
Valves
Pressure relief devices
Sampling connections
Flanges, screwed connections, etc.
Open-ended lines
Drains, vents, doors
Agitator seals

Service
Gas/vapor
Light liquid
Heavy liquid

effectively treated as separate streams. If the emission estimate is being generated in support of control strategies for individual chemical compounds, this approach offers the advantage of screening groups of equipment components with roughly the same composition of materials in the line.

Each source should be uniquely identified to indicate that it has been screened. For example, sources can be tagged. Tags can consist of any form of weatherproof and readily visible identification. Alternatively, a process unit can be considered appropriately tagged if the unit has a system of identifying markings with an associated diagram allowing easy location of marked sources. Once all the equipment along the major streams has been screened, the unit should be divided into a grid to search for fittings missed on the initial survey. The unit survey is completed when all sources in the unit have been either screened or identified as a nonhydrocarbon fitting. Leakless equipment and equipment not in VOC (or VHAP) service should not be included in the screening survey. Equipment documented as inaccessible should be included in the survey; such equipment must be screened annually under regulations for fugitive emissions.

Consistent with equipment leaks standards for hazardous air pollutants, unsafe-to-monitor equipment do not need to be included in the survey. Documentation must be provided, however, to substantiate the unsafe nature of such equipment.

3.2 MONITORING INSTRUMENT

A number of portable VOC detection devices are capable of measuring leaks from process units. These devices operate on a variety of principles, the three most common being ionization, infrared absorption, and combustion. Any analyzer can be used provided it meets the specifications and performance criteria set forth in EPA Reference Method 21.[1] Reference Method 21 is included in this document as Appendix A. Any analytical instruments are permitted provided they are shown to measure the organic compounds of interest and the results are related to EPA's data base generated using a flame ionization detector, calibrated to methane. Analytical instruments referenced to compounds other than methane must develop response factors to relate screening values to concentration. This will allow use of many instruments that cannot be calibrated with methane.

3.2.1 Operating Principles and Limitations of Portable VOC Detection Devices

Ionization detectors operate by ionizing the sample and then measuring the charge (number of ions) produced. Two methods of ionization currently used are flame ionization and photoionization.

A standard flame ionization detector (FID) usually measures the total carbon content of the organic vapor sampled. Although carbon monoxide and carbon dioxide do not produce interferences, FID analyzers do react to water vapor, although at a low sensitivity. Furthermore, if water condenses in the sample tube, erratic readings may result. A filter is used to remove particulate matter from the sample. When equipped with options, certain portable FID instruments are capable of measuring total gaseous nonmethane organics or individual organic components. Certain organic compounds containing nitrogen, oxygen, or halogen atoms when sampled with an FID give a reduced response; and some organics may not give any response at all. For this reason, it is necessary to develop response factors for each compound that is to be measured. Response factors are discussed in Section 3.2.2.1.

Photoionization detectors use ultraviolet light (instead of a flame) to ionize organic vapors. As with FID's, the detector response varies with the functional group in the organic compounds. Photoionization detectors have been used to detect leaks in process units used in the synthetic organic chemical manufacturing industry, especially for certain compounds such as formaldehyde that will not give a response on an FID or combustible detector.

Nondispersive infrared (NDIR) instruments operate on the principle of light absorption characteristics of certain gases. NDIR instruments are usually subject to interference because other gases such as water vapor and carbon dioxide may also absorb light at the same wavelength as a compound of interest. These detectors are generally used only for the detection and measurement of single components. For the detection and measurement of single components, the wavelength at which a certain compound absorbs infrared radiation is predetermined and the device is preset for that specific wavelength by using optical filters. For example, if set to a wavelength of 3.4 micrometers, infrared devices can detect and measure petroleum fractions, including gasoline and naphtha.

Combustion analyzers are designed either to measure the thermal conductivity of a gas or to measure the heat produced by combusting the gas. The most common method used in portable VOC detection devices is measuring the heat of combustion. These devices are referred to as hot wire detectors or catalytic oxidizers. Combustion analyzers, like most other detectors, are nonspecific for gas mixtures. In addition, combustion analyzers exhibit reduced response (in some cases, no response) to gases that are not readily combusted, such as formaldehyde and carbon tetrachloride.

3.2.2 Performance Criteria and Evaluation for Portable VOC Detectors

As previously stated, any portable VOC detector may be used as a screening device directly provided it meets the performance criteria specified in Reference Method 21 (see Appendix A). Although this approach has been shown to be applicable to many organics, it cannot be universally applied. Facilities may need to develop an appropriate method for testing inorganic and some organic compounds. A discussion of the performance criteria and detector evaluation procedure is presented below and summarized in Table 3-2.

In addition to the performance criteria, Reference Method 21 also requires that the analyzer meet the following specifications:

- The VOC detector shall respond to those organic compounds being processed (determined by the response factor).
- The analyzer shall be capable of measuring the leak definition specified in the regulation (i.e., 10,000 ppmv or "no detectable limit").
- The scale of the analyzer shall be readable to $\pm$5 percent of the specified leak definition concentration.
- The analyzer shall be equipped with a pump so that a continuous sample is provided at a nominal flow rate of between 0.5 and 3.0 liters per minute.
- The analyzer shall be intrinsically safe for operation in explosive atmospheres.

Also, criteria for the calibration gases to be used are specified. Two or more calibration gases are required for analyzer performance evaluation. One is a zero gas which is air with less than 10 ppmv VOC. The other calibration gases, or reference gases, use reference compounds in air mixtures. The concentration of the reference gas should represent the range

TABLE 3-2. PERFORMANCE CRITERIA FOR PORTABLE VOC DETECTORS[a]

Criteria	Requirement	Time Interval
Instrument response factor	Must be <10 unless correction curve is used.	One time, before detector is put in service.
Instrument response time	Must be ≤30 seconds	One time, before detector is put in service. If modification to sample pumping or flow configuration is made, a new test is required.
Calibration precision	Must be ≤10% of calibration gas value	Before detector is put in service and at 3-month intervals or next use, whichever is later.

[a]Source: Reference Method 21.

of responses measured. For the purpose of developing unit-specific emission estimates, a reference gas for the appropriate range should be used.

3.2.2.1 Response Factor. The sensitivity of an analyzer varies, depending on the composition of the sample and concentration detected. The response factor (RF) helps to quantify the sensitivity for each compound. The response factor is defined by:

$$\text{Response Factor} = \frac{\text{Actual concentration of compound}}{\text{Observed concentration from detector}}$$

It is important to note that the response factor may be used as a guide to selecting an appropriate monitoring device. For example, from the data presented in Appendix B, it can be readily seen that in screening equipment in a process unit containing cumene, an FID can be used (RF = 1.87) directly, with no correction for response factor; while the catalytic oxidation detector cannot (RF has no value). Similarly, from the same data, neither of these devices would be capable of detecting leaks from a source containing carbon tetrachloride if response factor adjustments are not used.

Using response factors as a general guide to analyzer applicability is especially important when dealing with chemical mixtures, since many process streams in industrial plants are composed of mixtures of chemicals. One EPA study concluded that analyzer response factors for a chemical mixture fall between the responses expected for the pure components.[5] Therefore, if desired, an interpolated or weighted average can be used to predict the response for mixtures based on known responses for individual chemicals. If sufficient information on pure components is not available or if desired, the response factor of a mixture for a specific instrument may be determined experimentally in the laboratory. Such results should be well documented. For further information see EPA-600/2-81-110, Response of Portable VOC Analyzers to Chemical Mixtures,[5] and EPA-600/2-8-051, Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds.[4]

Response factors also may be used to correct screening value measurements gathered to estimate emissions when using an emission factor approach (e.g., leak/no-leak approach or three-strata approach). If using leak rate/screening value correlations, however, a standard curve covering the entire range of

screening values measured must be used. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources.[4,5,6] An analyzer's response factor for individual compounds to be measured must be less than 10 at or near the concentrations defining emission factors (e.g., 1,000 and 10,000 ppmv) to be acceptable. The response factor tests are required before placing the analyzer in service, but do not have to be repeated at subsequent intervals.

Response factors can be determined by the following method. First, the analyzer is calibrated using the reference gas. Then, for each organic species that is to be measured, a known standard in air is obtained or prepared. This mixture is then injected into the analyzer and the observed meter reading is recorded. The analyzer is then zeroed by injecting zero air until a stable reading is obtained. The procedure is repeated by alternating between the mixture and zero air until a total of three measurements is obtained. A response factor is calculated for each repetition and then averaged over the three measurements.

Alternately, if response factors have been published for the compounds of interest for the combination of detector and calibration gas desired, the response factor determination is not required, and existing results may be referenced. Results of a study developing response factors of FID (Foxboro OVA-108 and OVA-128) and catalytic oxidation (J. W. Bacharach TLV Sniffer) analyzers are presented in Table B-1 of Appendix B.[4] These response factors can be used when determining if a screening concentration is above or below 10,000 ppmv. The values are for pure organic chemicals only. Table B-2 of Appendix B presents tested compounds that appear unable to achieve an instrument response of 10,000 ppmv at any feasible concentration unless response factors are used.[4] These single response factors are adequate for response factor adjustments when using one of the emission factor approaches for estimating emissions. When applying correlations, however, an accurate correction for the non-linear response of an instrument is needed. Response factors must be evaluated at several concentrations to establish a correction curve for use in translating instrument readings.

3.2.2.2 Response Time. The response time of an analyzer is defined as the time interval from a step change in VOC concentration at the input of a

sampling system, to the time at which 90 percent of the corresponding final value is reached as displayed on the analyzer readout meter. The response time must be equal to or less than 30 seconds. The response time must be determined for the analyzer configuration that will be used during testing, and the response time test is required before placing an analyzer in service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

3.2.2.3 Calibration Precision. Calibration precision is the degree of agreement between measurements of the same known value. To ensure that the readings obtained are repeatable, a calibration precision test must be completed before placing the analyzer in service, and at three-month intervals, or at the next use, whichever is later. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

To perform the calibration precision test, a total of three measurements is required for each nonzero concentration. Measurements are made by first introducing zero gas and adjusting the analyzer to zero. The specified calibration gas (reference) is then introduced and the meter reading is recorded. The average algebraic difference between the meter readings and the known value of the calibration gas is then computed. This average difference is then divided by the known calibration value and multiplied by 100 to express the resulting calibration precision as percent.

3.2.2.4 Safety. Portable instruments to detect VOC emissions from equipment leak sources are required to be used in hazardous locations such as petroleum refineries and bulk gasoline terminals. The National Electrical Code requires that instruments to be used in hazardous locations be certified to be explosion-proof, intrinsically safe, or purged.

Hazardous locations are divided into three classes: Class I, Class II, and Class III. Each class is divided into two divisions (Division 1 or 2) according to the probability that a hazardous atmosphere will be present; and also into seven groups depending on the type of hazardous material exposure. Groups A through D are flammable gases or vapors, and Groups E, F, and G apply to combustible or conductive gases. Class I, Division 1, Groups A, B, C, and D locations are those in which hazardous concentrations of flammable gases or

vapors may exist under normal operating conditions. Class I, Division 2, Groups A, B, C, and D locations are those in which hazardous concentrations of flammables may exist only under unlikely conditions of operation.

As of 1982, five manufacturers produced portable VOC detection instruments that are certified to be intrinsically safe. Table 3-3 lists these manufacturers, approved instrument model numbers, instrument certification categories, and performance specifications. Additionally, newer instruments may be available that meet the performance requirements for generating emission estimates.

3.2.3 Monitoring Devices For Difficult Situations

In some cases, a monitoring device may not be available that meets all of the performance specifications of Method 21. For example, there are several cases (e.g., phosgene) where the response factor at 10,000 ppmv is greater than ten (10). The instrument may meet all other requirements, but fails as a Method 21 instrument because it cannot meet the response factor requirement. The instrument can still be used to estimate emissions from equipment leaks, provided the instrument is shown to be sufficiently reliable in providing data that can be related to EPA's data collected using an OVA calibrated to methane.

Several steps must be taken initially to document the viability of a device that fails to meet the Method 21 requirements. First, a laboratory program must be undertaken to demonstrate the response of the monitoring instrument to the compounds being measured. This response must be documented. The second step involves relating the instrument response (i.e., screening value) to actual concentrations, or in other words, developing an instrument response curve. The screening value response curve must be developed for the entire screening value range and documented so that screening values taken in the field can be adjusted to actual concentrations. Third, the testing program should be sufficiently well documented to demonstrate how the instrument will be used in screening equipment. For example, if the response time of the candidate instrument exceeds the Method 21 performance specification, the test plan should reflect added screening time at each potential leak point to be screened. Once this laboratory demonstration has been completed and the screening value correction curve has been established, the screening can begin.

TABLE 3-3. PORTABLE VOC DETECTION INSTRUMENT PERFORMANCE SPECIFICATIONS

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Range (ppm)	Certification
Bacharach Instrument Co., Santa Clara, California	L	Combustible gases	Catalytic Combustion	0-100% LEL	Intrinsically safe, Class I, Division 1, Groups C and D
	TLV Sniffer	Combustible gases	Catalytic Combustion	0-1,000 and 0-10,000	Intrinsically safe, Class I, Division 1, Groups C and D; and Class I, Division 2, Groups A and B
Foxboro, S. Norwalk, Connecticut	OVA-128	Total hydrocarbons	FID/GC	0-1,000	Intrinsically safe, Class I, Division 1, Groups A, B, C and D
	OVA-108	Total hydrocarbons	FID/GC	0-10,000	Intrinsically safe, Class I, Division 1, Groups A, B, C and D
HNU Systems, Inc. Newton Upper Falls, Massachusetts	PI-101	Chlorinated hydrocarbons, aromatics, aldehydes, ketones, any substance which UV light ionizes	Photo-ionization	0-20, 0-200, 0-2,000	Intrinsically safe, Class I, Division 2, Groups A, B, C and D
Mine Safety Appliances Co., Pittsburgh, Pennsylvania	40	Combustible gases	Catalytic Combustion	0-10% and 0-100% LEL	Intrinsically safe, Class I, Division 1, Group D; and Class I, Division 2, Groups A, B, and C
Survey and Analysis, Inc., Northboro, Massachusetts	On Mark Model 5	Combustible gases and vapors	Thermal Conductivity	0-5 and 0-100% LEL	Intrinsically safe, Class I, Division 1, Groups A, B, C and D

3.3 SCREENING PROCEDURES

3.3.1 Calibration Procedures

Pretest procedures to be followed include calibration of the monitoring instrument. The VOC analyzer should be assembled and started up according to the manufacturer's instructions. After the appropriate warm-up period and zero internal calibration procedure, the calibration gas is introduced into the sample probe. The instrument meter readout is then adjusted to correspond to the calibration gas value. If the meter readout cannot be adjusted to the proper value, a malfunction of the instrument is indicated and corrective measures should be taken before use.

3.3.2 Procedure for Screening Equipment

The mechanics of the screening operation outlined in Reference Method 21 are summarized in the following discussion. The probe inlet is placed at the surface of the leak interface where leakage could occur. (The leak interface is the boundary between the process fluid and the atmosphere.) Care must be taken to ensure that the probe is held perpendicular, not tangential, to the leak interface. Otherwise, inaccurate readings will result. The probe must then be moved along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly move the probe along the interface where leakage is indicated until the maximum meter reading is obtained. The probe inlet should be left at this maximum reading location for approximately two times the instrument response time. The maximum reading is recorded as the screening value.

The instrument measurement may exceed the scale of the instrument. For example, the reading may exceed 10,000 ppmv when using an OVA analyzer. For the purposes of generating an emission estimate, these higher readings also must be recorded. A dilution probe should be employed to allow measurement of concentrations greater than the instrument's normal range. The OVA can be equipped with a dilution probe that permits measurement of concentrations up to 100,000 ppmv. It is important to note that extending the measurement range also necessitates the calibration of the instrument to the higher concentrations.

Care should be taken to avoid fouling of the probe with grease, dust, or even liquids. A short piece of Teflon tubing can be used as a probe tip

extender and snipped off as the tip fouls. In areas with a noticeable particulate loading, this tubing can be packed with untreated fiberglass to act as a filter. (Note that the instrument must also be calibrated with this filter in place). If a surface to be screened is obviously dirty, hold the probe tip just over the surface to avoid scooping up contaminants. Some fouling is unavoidable, so it is recommended that the probe tip sintered steel filter be cleaned at least daily and the side-pack filter on a weekly basis. Normally, these filters can be cleaned by just rapping them lightly on a table top, but if the deposits are wet and caked on, washing with an aqueous solution of soap and alcohol is recommended. This can also be used to wash the probe and transfer line periodically. Care should be taken to blow the equipment dry before reuse.

This general procedure can be used to screen equipment such as valves, flanges, pumps and compressors, pressure relief devices, and other potential sources of VOC leakage such as process drains and open-ended lines or valves.

For valves, the most common source of leaks is at the seal between the stem and housing. To screen this source, the probe is placed where the stem exits the packing gland. The probe is moved around the stem circumference. The maximum reading is recorded as the screening value. Also, the probe is placed at the packing gland take-up flange seat and the probe is moved along the periphery. In addition, valve housings of multipart assemblies should be screened at the surface of all points where leaks could occur. Figures 3-1 through 3-5 illustrate screening points for several different types of valves.

For flanges, the probe is placed at the outer edge of the flange-gasket interface and the circumference of the flange is sampled. For screwed flanges, the threaded connection interface must also be screened. Other types of nonpermanent joints, such as threaded connections, are sampled with a similar traverse.

Pumps and compressors are screened with a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface where the shaft exits the housing. If the source is a rotating shaft, the probe inlet is positioned within 1 cm of the shaft-seal interface. If the housing configuration prevents a complete traverse of the shaft periphery, all accessible portions must be sampled. All other joints on the pump or

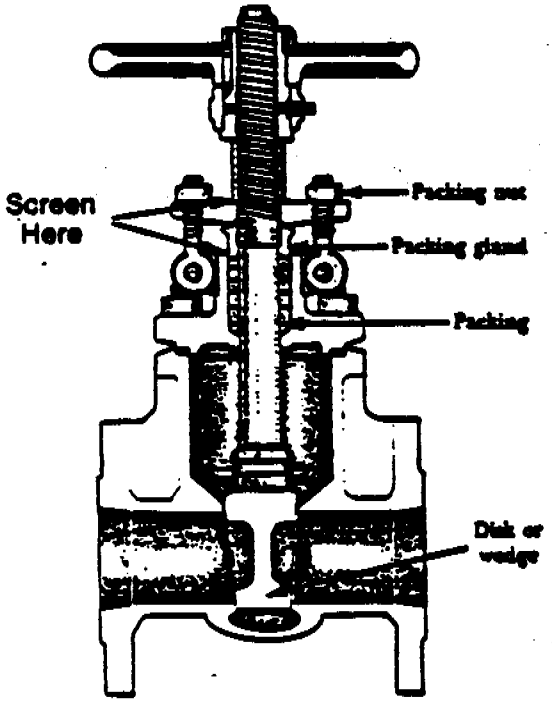


Figure 3-1a. Rising stem type.

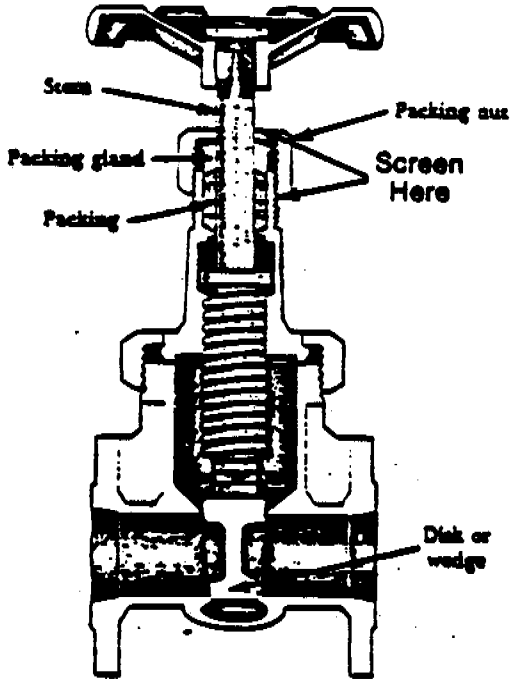


Figure 3-1b. Non-rising stem type.

Figure 3-1. Gate valves.

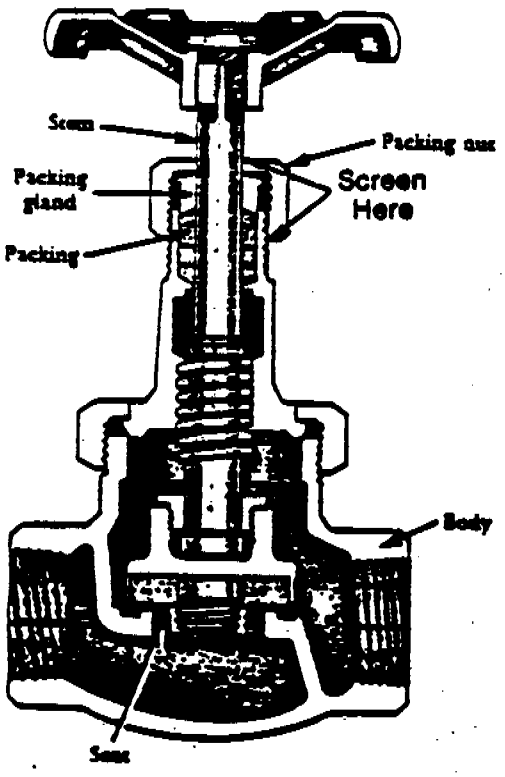


Figure 3-2a. Manual Globe Valve

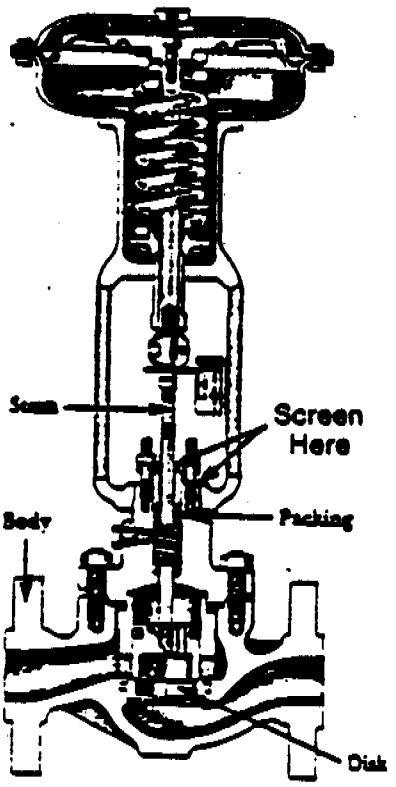


Figure 3-2b. Globe type control valve

Figure 3-2. Globe valves.

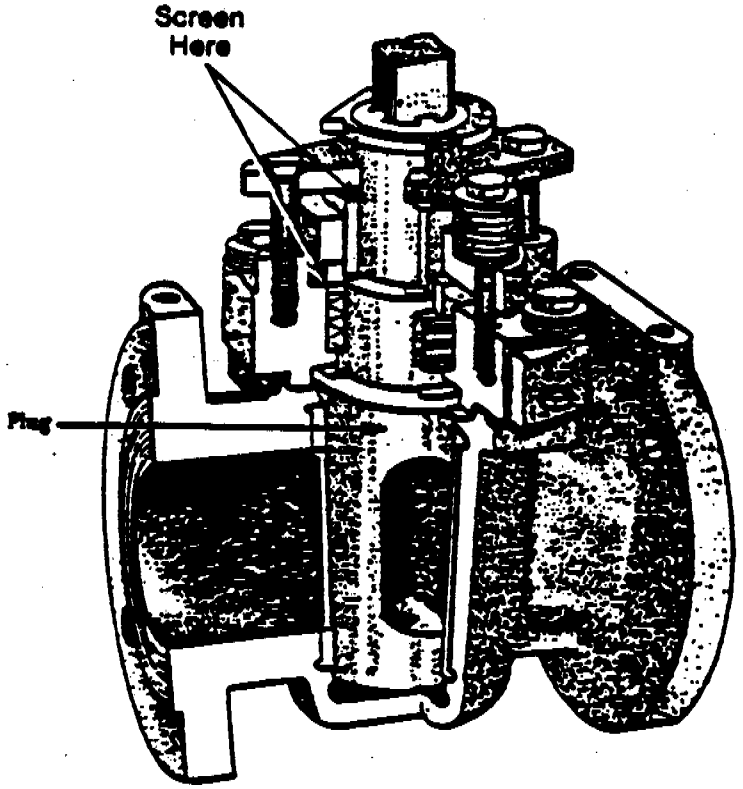


Figure 3-3. Lubricated plug valve.

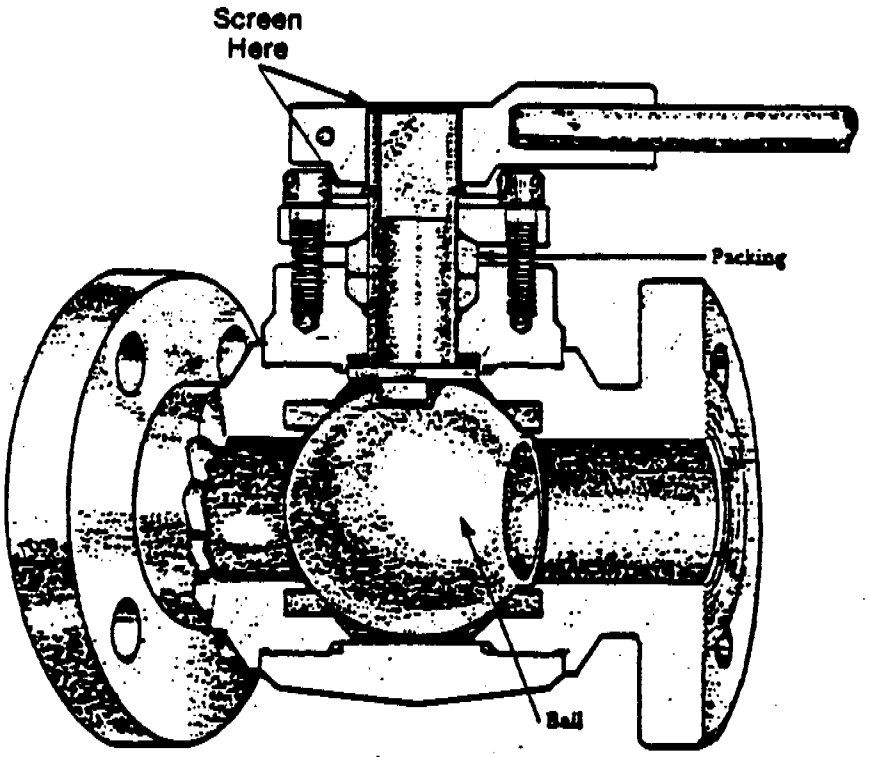


Figure 3-4a. Ball valve.

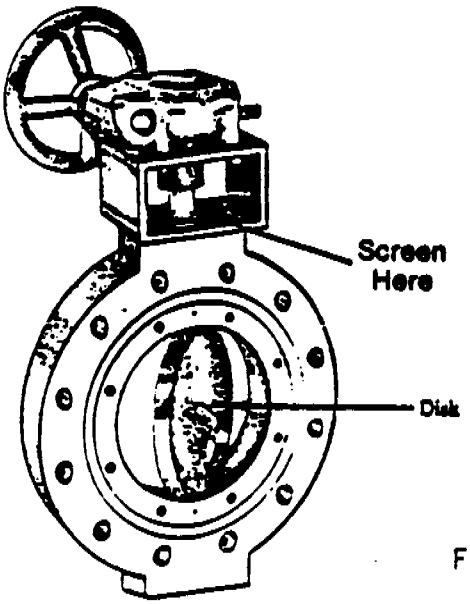


Figure 3-4b. Butterfly valve.

Figure 3-4.

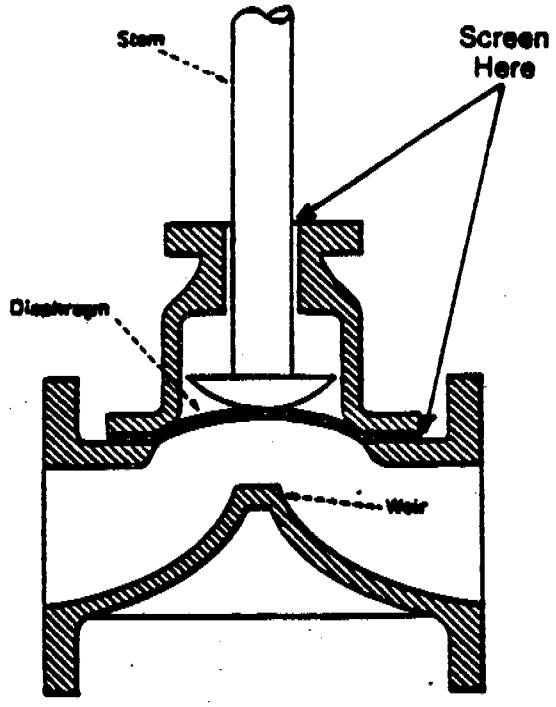


Figure 3-5a. Weir type diaphragm valve.

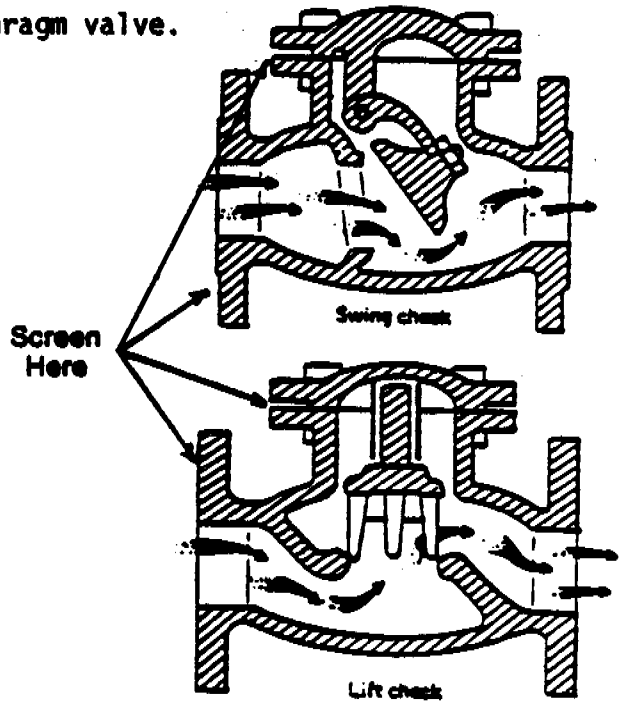


Figure 3-5b. Check valves.

Figure 3-5.

compressor housing where leakage could occur should also be sampled. Figure 3-6 illustrates screening points for two types of centrifugal pumps. Agitator seals should be screened in a similar manner.

The configuration of most pressure relief devices prevents sampling at the sealing seat. Because of their design and function, pressure relief devices must be approached with extreme caution. These devices should not be approached during periods of process upsets, or other times when the device is likely to activate. Similarly, care must be used in screening pressure relief devices to avoid interfering with the working parts of the device (e.g., the seal disk, the spring, etc.) For those devices equipped with an enclosed extension, or horn, the probe inlet is placed at approximately the center of the exhaust area to the atmosphere. Again, only the probe should be placed in the horn; personnel conducting the screening should not place hands, arms, or any parts of the body into the horn. Figure 3-7 illustrates the screening points for a spring-loaded relief valve.

Fugitive leaks from most other sources such as process drains, open-ended lines or valves, and seal system degassing vents and accumulator vents, are emitted through a regularly shaped opening. If that opening is very small (as in sampling lines of less than one inch diameter), a single reading in the center is sufficient. For larger openings (like a six inch drain mouth), it is necessary to traverse the perimeter of the opening. The concentration at the center must also be read. For even larger sources (like a wash-up drain grate), a grid of readings should be taken on about six inch centers. For access door seals, the probe inlet is placed at the surface of the door seal for the peripheral traverse. For all of these types of equipment, it is the maximum value that is recorded as the screening concentration.

3.4 DATA HANDLING

To handle the screening data uniformly, it is recommended that data be recorded on prepared data sheets. The data collected should include the following:

1. Date.
2. Hydrocarbon detector type.
3. Source identification. (If permanent ID's are not in place, assign ID's consecutively as each source is screened. The first source screened is assigned ID1, the second source screened, ID2, and so on.)

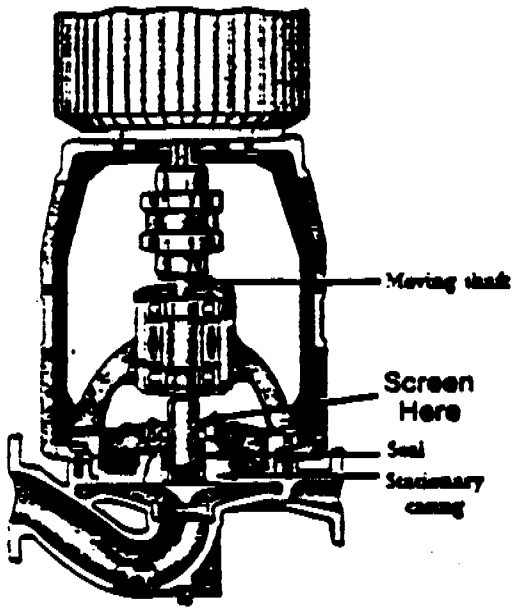


Figure 3-6a. Vertical centrifugal pump.

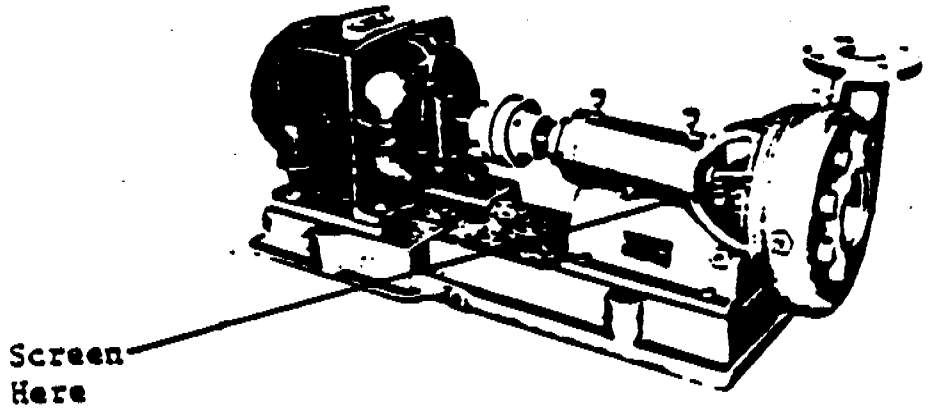


Figure 3-6b. Horizontal centrifugal pump.

Figure 3-6.

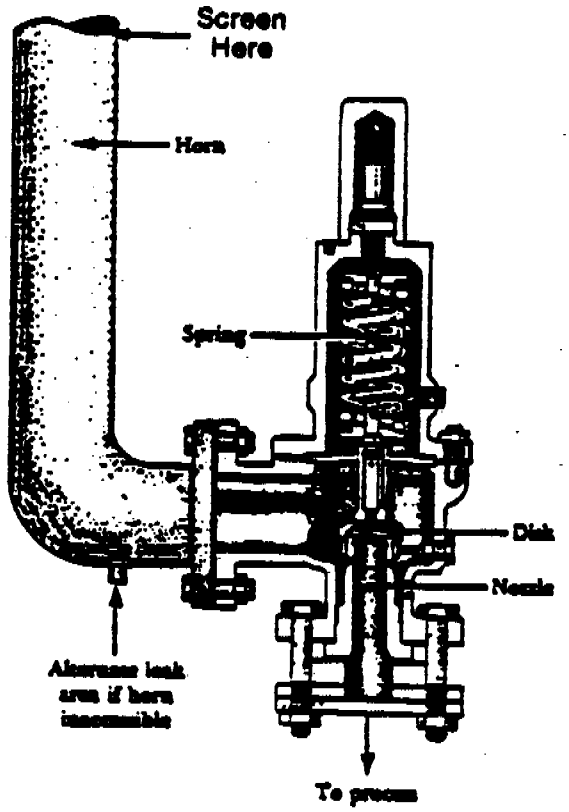


Figure 3-7. Spring loaded relief valve.

4. Screening value recorded in ppmv.

5. Source type (i.e., type of valve, pump, compressor, flange, etc.)

6. Service. For example, gas, light liquid, and heavy liquid. Liquids are classified based on their most volatile component present at 20 weight percent or more. If the components have a total vapor pressure equal to or greater than 0.04 psi at 20°C, the material (containing greater than or equal to 20 percent VOC) is classified as a light liquid; if not, it is classified as a heavy liquid. Classification is based upon the actual process conditions, not ambient conditions.

7. Comments. If any explanation is required, it should be noted in a "comments" section. An example data sheet is given in Table 3-4.

In some cases, it may be necessary or desirable to adjust the screening values for response factor. In these cases, the data sheet should be designed to accommodate extra columns for response factor and corrected screening values.

3.5 CALIBRATION PROCEDURES FOR QUALITY ASSURANCE

Calibration procedures must be used for quality control to ensure the collected data are of high quality and can be compared to the data already gathered by EPA.

Each screening instrument should be checked for calibration before each use and readings from these checks recorded. As an example, instruments should be calibrated each morning before use and before use in the afternoon. The calibration should also be checked periodically (such as during breaks in the daily testing schedule) to ensure that calibration has not drifted. The instruments should be calibrated if the reading is off by more than $\pm$5% on the high standard, or $\pm$20 on the low standard. If more than one instrument is being used at one process unit, the calibration readings for all instruments must be recorded.

TABLE 3-4. EXAMPLE DATA SHEET

Date	Hydrocarbon Detector Type	Source ID	Screening Value (ppmv)	Process Unit	Service	Primary Material	Comments

SECTION 4.0
MASS EMISSIONS SAMPLING

The process of measuring organic concentrations at potential leak points of equipment when combined with the EPA's leaking and non-leaking emission factors gives a good estimate of the leak rate from a process unit. More rigorous procedures may be used to determine the mass emission rate more accurately. Measuring mass emission rates requires source enclosure combined with sampling of the gas in the enclosure. The dilution or vacuum method is the preferred technique for sampling the emissions from sources that can be enclosed. An alternate sampling technique is the blow-through method which is usually used for sources with very large leak rates (in excess of the vacuum pump capacity). An important step in either of these methods, however, is source enclosure, a procedure called bagging.

4.1 VACUUM METHOD

In the past, the method preferred for sampling leaks from baggable sources has been the dilution or vacuum method. The sampling train used in this method is shown in Figure 4-1.

The train can be mounted on a portable cart, which can be easily moved around the process unit from source to source. The major equipment items in the sampling train are the vacuum pump used to draw air through the system, and the dry gas meter used to measure the flow rate of gas through the train. In previous studies that EPA conducted, a 4.8 CFM Teflon-ring piston type vacuum pump equipped with a 3/4-horsepower air-driven motor was used. Low pressure air (~100 psig) is available at or near most process units. An example of a suitable dry gas meter is a Rockwell Model 1755 Test Gas Meter with a Number 83 Test Index.[12] Other equipment that EPA used in the train includes Whitey valves, copper and stainless steel tubing, Teflon tubing, 100 cc glass airtight syringe, thermometers, mercury and water manometers, a cold trap, and an air-driven diaphragm sampling pump.

The leak source is shown as a valve in Figure 4-1. However, the same sampling train can be used for all equipment to be sampled using the vacuum technique. As described in Section 4.3, the size and shape of the enclosure (tent) around the potential leak point is adjusted to fit the particular shape

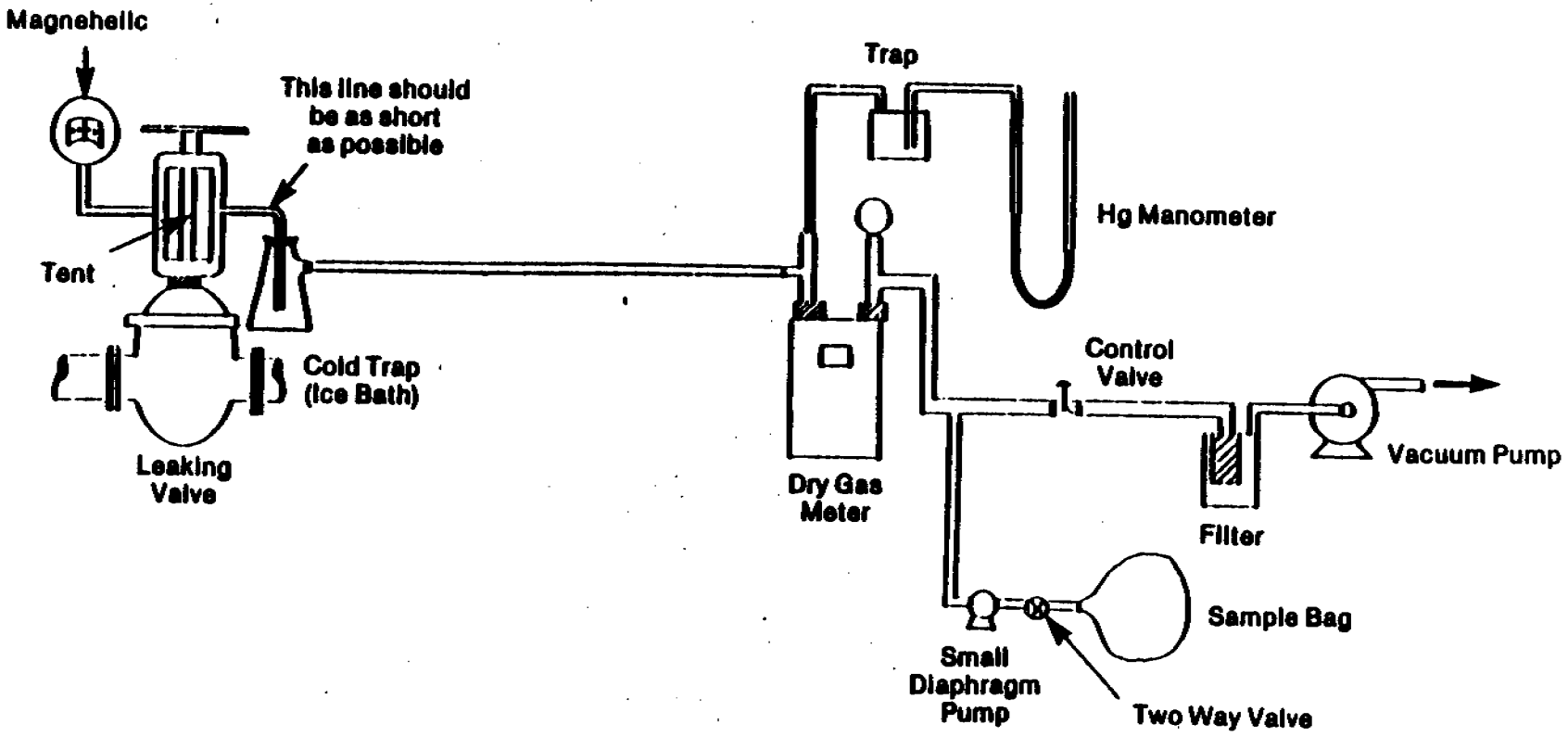


Figure 4-1. Sampling train for baggable sources of hydrocarbon emissions using a diaphragm.

and operating condition of the equipment. When the full sampling train is connected, the vacuum pump is able to maintain a maximum flow rate of approximately 2.5 cubic feet per minute (0.001 cubic meters per second).

The tent is connected by means of a bulkhead fitting and Teflon tubing to the sampling train. A separate line is connected from the tent to a magnahelic to allow continuous monitoring of the pressure inside of the tent. If a significant vacuum exists inside the tent when air is being pulled through, a hole is made in the opposite side of the tent from the outlet to the sampling train. This allows air to enter the tent more easily and thus reduces the vacuum in the enclosure. In practice, it has been found that only a very slight vacuum (0.1 inches H_2O) is present in the tent during most of the sampling, even in the absence of a hole through the tent wall. Sufficient air enters around the seals to prevent the development of a significant vacuum in the tent. Sample bags are used to collect gas samples and transport them to the laboratory for analysis. As with the tent material, sample bags must be constructed of material that is impermeable to hydrocarbons so that the process components are contained within the sample bag. Mylar plastic, Teflon, and Tedlar are materials well suited to this function. A typical sample bag is shown in Figure 4-2.

A cold trap is placed in the system to condense water and heavy organics, thus preventing condensation in downstream lines and equipment. The cold trap can be simply a 500 ml flask in an ice bath placed as close as possible to the tent. While not always necessary, this ice bath cold trap is very effective in preventing condensation in the remainder of the sampling train and in the gas sample bag. Any organic condensate that collects in the cold trap must be measured for later use in calculating total leak rates. On some streams the use of a cold trap is critical.

The flow rate through the system can be varied by throttling the flow with a control valve immediately upstream of the vacuum pump. As the flow rate is decreased, the concentration of hydrocarbon increases in the gas flowing through the sampling system. This allows considerable flexibility in avoiding operations with an explosive mixture of hydrocarbon in the air. If an explosive mixture is present, the blow-through method should be used.

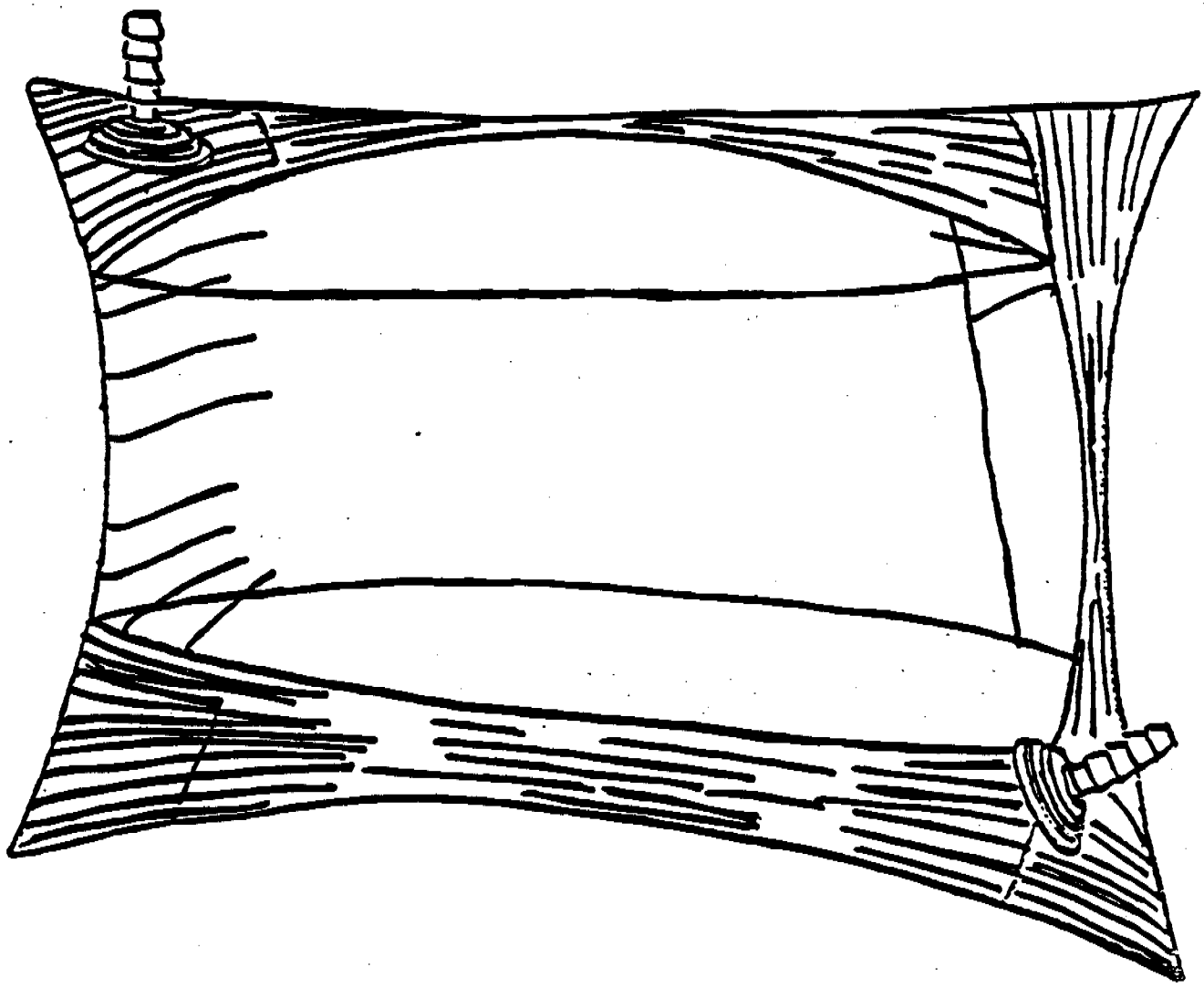


Figure 4-2. Mylar plastic sample bag.

In summary, the vacuum sampling procedure consists of the following steps:

- Obtain and record a screening value with the portable hydrocarbon detector,
- Enclose the source in a tight shroud,
- Connect the tent to the sampling train,
- Immerse the cold trap in an ice bath,
- Note the initial reading of the dry gas meter,
- Start the vacuum pump and a stopwatch simultaneously,
- Record the temperature and pressure at the dry gas meter,
- Observe the VOC concentration at the vacuum pump exhaust with the hydrocarbon detector,
- Record the temperature, pressure, dry gas meter reading, outlet VOC concentration and elapsed time every 2 to 5 minutes,
- Fill a gas sample bag from the discharge of the Teflon-lined diaphragm pump when the outlet VOC concentration stabilizes (i.e., the system is at equilibrium),
- Fill another bag with ambient air near the tent area to detect the background VOC concentration,*
- Take a final set of readings and stop the vacuum pump,
- Remove, seal, and transport the cold trap is to the laboratory along with the two bag samples and the data sheet,
- Remove the tent,
- Rescreen the source with the portable hydrocarbon detector and record.

All of the above data and any pertinent comments should be recorded in a permanent laboratory notebook.

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*This bag sample may be omitted in favor of the hydrocarbon detector reading if the background VOC concentration is less than 5 percent of the lower limit of the screening range (i.e., <50 ppm for the 1,000 to 10,000 ppm class). When bagging a "zero" screening value component, it is extremely important to take a background bag. Data obtained without a background ag will bias emission factors on the high side unless this correction is m e.

4.2 BLOW-THROUGH METHOD[a]

Blow-through refers to blowing nitrogen through a flexible tent to create a constant VOC concentration inside the tent. Nitrogen is metered into the tent through 1 or 2 polyvinyl chloride tubes. The temperature and oxygen concentrations are measured inside the tent with a platinum-RTD thermocouple and an oxygen/combustible gas monitor. The flow of nitrogen is monitored in a gas rotameter calibrated to nitrogen. The nitrogen passes though activated charcoal and drierite to remove any organics and moisture. The pressure in the tent never exceeds 1 psig. Figure 4-3 illustrates the equipment required for the blow-through method.

At least two OVA (Foxboro 108 Organic Vapor Analyzer) measurements are made inside the tent, each measurement at two or more differing nitrogen flow rates to increase accuracy. [The OVA must be attached to a dilution probe and calibrated to nitrogen-diluted gases to allow its use in the nitrogen atmosphere in the tent.] The OVA readings are converted to emission rates of VOC via response factors for the OVA; the calculation is shown in Table 4-1. Alternatively, gas samples from the tent can be collected with a portable sampling pump and transported to a lab for chemical speciation and concentration measurement. The calculation in Table 4-1 is also applicable for concentrations measured in this manner (except that the response factor is set equal to 1).

The oxygen concentration is also measured to determine the total gas flow rate through the tent. However, oxygen concentration is also used to rate the quality of the tent, and except for a few extremely difficult situations, VOC concentrations are not measured until the oxygen concentration in the tent is reduced below 5%.

Air can replace nitrogen as a dilution gas if the hydrocarbon concentration is not expected to be high enough to cause an explosive atmosphere inside the tent. However, calculations based on air tent data must assume a nominal tent leakage rate, i.e., extra flow through the tent due to air entering the tent that is not metered through the tubing.

Safety has been a key factor in the development of this procedure. Over 400 valves have been tented with this technique without incident. Nitrogen is

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[a]Text adapted from Chemical Manufacturers Association, Guidance for Estimating Fugitive Emissions, July, 1987.

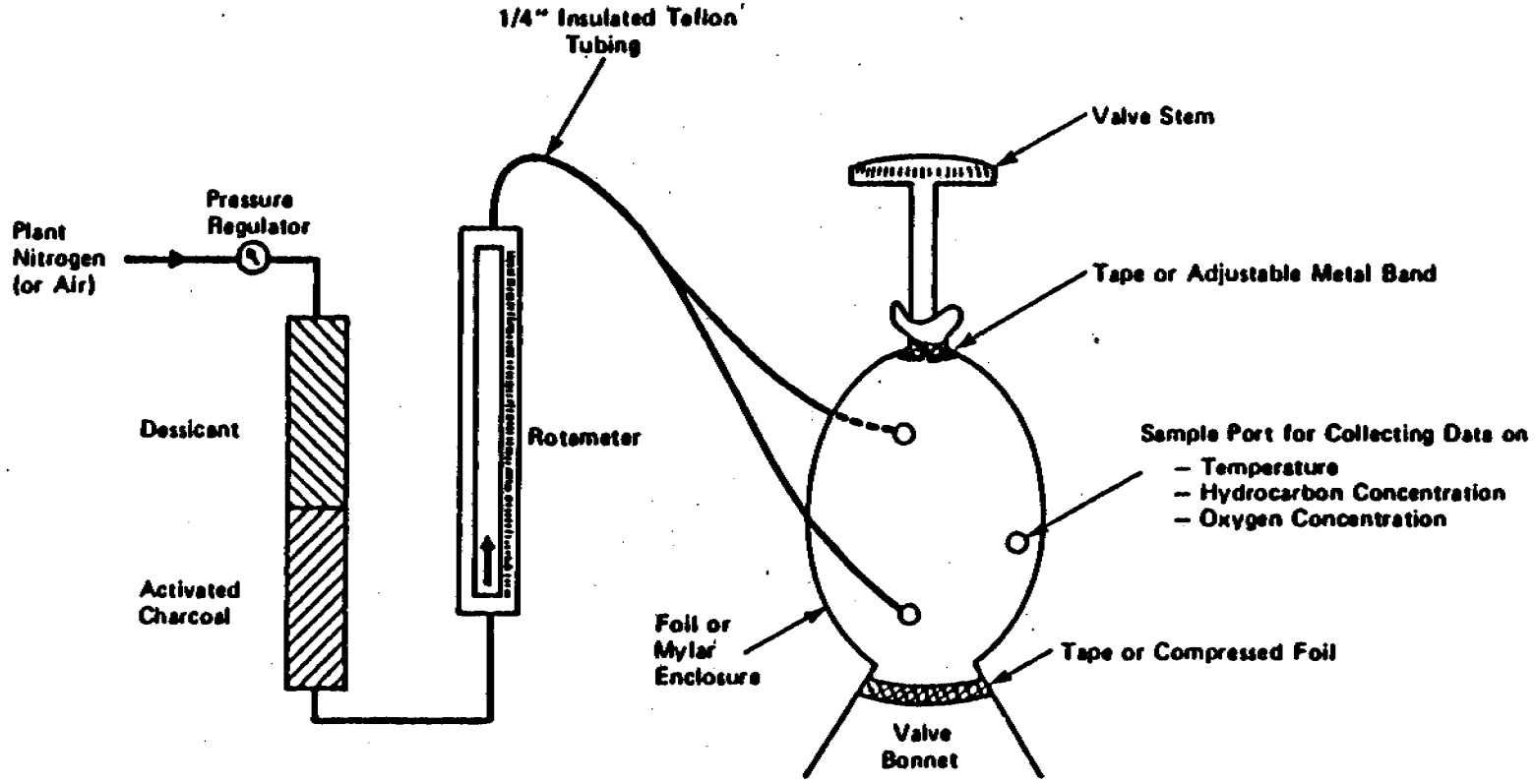


Figure 4-3. Equipment required for the blow-through sampling technique.

TABLE 4-1. CALCULATION PROCEDURES FOR TENTED LEAK RATE

$$\text{Tent rate (lb/hr)} = \frac{4.836 \times 10^{-5}\,(Q)(MW)(OVA)(RF)}{T + 460}$$

where

Q = flow rate into tent in cubic meters/hour

$$= \frac{N_2 \text{ flow rate in liters/minute}}{1 - \left(\frac{\text{tent oxygen concentration in \%}}{21}\right)} \left[0.06 \frac{m^3\text{-minute}}{\text{liter-hour}}\right]$$

MW* = molecular weight of gas in pounds/pound-mole

T = temperature in tent in ^{o}F

OVA = instrument reading minus background reading, in vppm

RF** = response factor for leaking gas relative to calibration gas

4.836×10^{-5} = a conversion factor taking into account the gas constant and assuming a pressure in the tent of 1 atmosphere

*For mixtures:
gas molecular weight = (mole fraction-gas 1)(molecular weight-gas1) +
(mole fraction-gas 2)(molecular weight-gas 2) + ...

**For mixtures:
gas response factor = (mole fraction-gas 1)(response factor-gas 1) +
(mole fraction-gas 2)(response factor-gas 2) + ...

where response factor is calculated at the OVA concentration. For liquid mixtures, a detailed analysis based on vapor-liquid equilibrium must be done to use OVA concentrations.

used as a dilution gas instead of air to prevent an explosive atmosphere within the tent. All of the instruments used are battery-operated and approved for Class I, Division I use. In summary, the blow-through method consists of the following steps:

- Interview the unit operator to determine the composition of the material in the designated equipment component (in weight or volume %), and the operating conditions of the component.
- Screen the component by placing a Tygon nozzle on the end of the Foxboro/Century OVA (Organic Vapor Analyzer), holding the end of the nozzle within 1 centimeter of the leak interface, and recording the highest concentration seen on the OVA readout.
- Cut a tent from appropriate material (see section 4.3 - Source Enclosure) that will easily fit over the equipment component.
- Connect tubing from the nearest low pressure nitrogen station to a rotameter stand, which includes a regulator, dessicant, activated charcoal, and a rotameter in series.
- Run tubing from the rotameter outlet to a "Y" that splits the nitrogen flow into two pieces of tubing. Insert the tubes into openings located on either side of the tent.
- Turn on nitrogen at the utilities station and regulate it at the rotameter to approximately 40 liters/minute.
- After the nitrogen is flowing, wrap aluminum foil around those parts of the equipment component where air could enter the tent-enclosed volume.
- Use duct tape, wire, and/or rope to secure the tent to the component.
- Put a third hole in the tent roughly equidistant from the two nitrogen-fed holes.
- Measure the oxygen concentration in the tent by inserting the lead from an O_2 meter into the third hole. Adjust the tent (add additional tape, foil, rope, etc.) until the O_2 concentration is less than 5%.
- Measure the temperature in the tent with a platinum-RTD thermocouple.
- Calibrate the OVA to methane or hexane at a known concentration in nitrogen using the OVA dilution probe. Remember to correct for the dilution before inserting the OVA concentration reading into the calculation in Table 4-1.

- Check the VOC concentration at several points in the tent with the OVA to insure that the tent contents are at steady state.

- Measure the hydrocarbon VOC concentration in the tent with the OVA at three different nitrogen flow rates. Typically the flow rates will be 40, 30 and 20 liters/minute if there is no OVA response at the higher rates (i.e., the mass leak rate from the component is very low). After each adjustment of the nitrogen flow, check the O_2 concentration to ensure it stays below 5%. Alternatively, collect samples in Tedlar or aluminized sample bags by drawing sample out of the bag with a portable sampling pump.

- Remove the tent and any plugs from the component and collect any condensate on the inside of the tent in a plastic graduated cylinder. Record the amount collected and the elapsed time the tent was on the component.

- If there is liquid dripping from the component, collect the drips for a timed period which produces enough collected material for accurate volume measurement. Record the amount in the report, but do not add it to the vapor leak rate.

4.3 SOURCE ENCLOSURE

To measure the leak rate from any given fitting accurately, it is necessary to isolate that fitting from the ambient air. This is accomplished by an enclosure (or tent) formed around the leak source. Appropriate tent material must be selected, so that the substances found in the process fluid are contained within the tent. For example, because polyethylene is permeable to hydrocarbons, it is an inappropriate tent material. By comparison, Mylar plastic (polyethylene terephthalate) is well suited to this function as it does not absorb significant amounts of hydrocarbons, it is very tough, and it has a high melting point (250°C). Other suitable materials are Tedlar (PVF film) and Teflon (fluorocarbon resin). For convenience, Mylar will be used as an example of tent material in the following discussions. The thickness of the tent material can range from 1.5 to 15 mil depending on the type of equipment being bagged. A typical tent is shown in Figure 4-4. The enclosures should be kept as small as practical. This has several beneficial effects:

- the time required to reach equilibrium is kept to a minimum,
- the time required to construct the enclosure is minimized,
- a more effective seal results from the reduced seal area, and

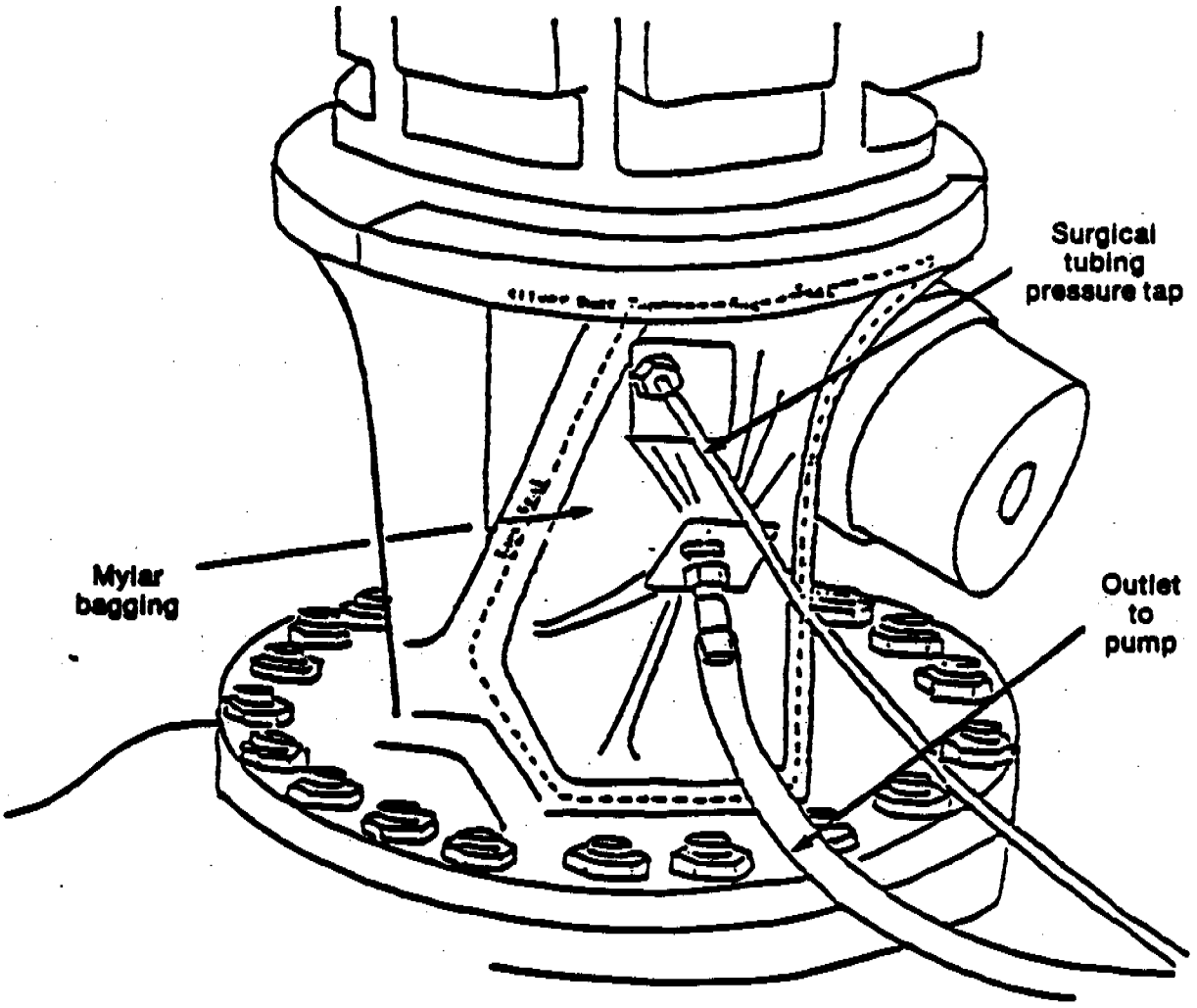


Figure 4-4. Tent construction around the seal area of a vertical pump.

- condensation of heavy hydrocarbons inside the enclosure is minimized or prevented due to reduced residence time and decreased surface area available for heat transfer.

Tent construction for individual sources is discussed in the sections 4.3.1 through 4.3.5.

4.3.1 Valves

The most important property of the valve that affects the type of enclosure (tent) selected for use is the metal skin temperature of the area enclosed by the tent and around which the seal is made.

At skin temperatures of 400°F or less, the valve stem and/or stem support can be wrapped with 1.5-2.0 mil Mylar and sealed at each end and at the seam with duct tape. A leak-tight seal is not required when the vacuum method of leak measurement is used. Actually, it is better to allow for some areas of incomplete sealing to provide access for air being drawn through the tent by the vacuum pump in the sampling train.

Two bulkhead fittings are then attached to the Mylar tent. One is for the water manometer or differential pressure gauge connection, and the other is for the line to the sampling train. If, after starting the sampling, a vacuum greater than 0.1 inches of water is found to exist in the tent, a hole can be added on the side of the tent opposite the outlet to the sampling train. This provides an additional entrance for the dilution air, and reduces the vacuum in the tent while sampling. The Mylar tent must be constructed to enclose the valve stem seal and the packing gland seal.

When skin temperatures are in excess of 400°F, other methods of tenting the valves can be used. In one method, adjusted metal bands or wires are wrapped around all hot points that are in contact with the Mylar tent material. Seals are then made against the insulation using duct tape or adjustable metal bands of stainless steel.

At extremely high temperatures, metal foil can be wrapped around the valve leak area. In a previous study, seals were made using adjustable metal bands.[11] At points where the shape of the equipment prevented a satisfactory seal with metal bands, the foil was crimped to make a seal. It was necessary, in some of these instances, to use a relatively high capacity vacuum pump to insure a constant inflow of air through all seal areas.

Mixed-phase valve leaks are enclosed with the same type of tent described above. The rate of leakage of liquid is measured by collecting it over a measured length of time. A low point is formed in the tent to collect the liquid so its volume can be measured and converted to a mass rate. The total mass leak rate can then be estimated by adding the liquid mass leak rate to the gas mass leak rate.

4.3.2 Pumps and Agitators

As with valves, the property of most concern when preparing to sample a pump or agitator is the metal skin temperature at areas or points that are in contact with the tent material.

At skin temperatures below 400°F, Mylar plastic and duct tape are satisfactory materials for constructing a tent around a pump or agitator seal. The vast majority of centrifugal pumps in VOC service have a housing or support that connects the pump drive (or bearing housing) to the pump itself. The two supports normally enclose about half of the area between the pump and drive motor, leaving open areas on the sides. It is usually a relatively simple matter to cut panels to fit these remaining open areas. In a previous study, the panels were cut from 14 mil Mylar.[11] Bulkhead fittings for the outlets to the water manometer and sampling train are placed through one Mylar panel and sealed. An opening (hole, bulkhead fitting) is made in the opposing panel, if necessary, to allow easier flow of dilution air into the enclosure around the seal.

In many horizontal pumps, there is a line from the bottom of the lower metal support to a drain. This line serves as a drain for coolant, sealant, and/or process liquid leaking from the pump seal. This line (and all other lines from the enclosure) should be sealed off to avoid drawing air and hydrocarbon vapors from the drain back up to the sealed enclosures. If there is no liquid flowing through this drain line, it can be plugged off. If liquid is going to the drain, a short length of hose or tubing can be attached to the end of the drain line and looped upward to form an effective liquid seal.

In the cases where supports are absent or quite narrow, a cylindrical enclosure around the seal can be made so that it extends from the pump housing to the motor or bearing support. This enclosure can be made of 14 mil Mylar, since this thickness provides considerable strength and rigidity.

Reciprocating pumps present a somewhat more difficult tenting problem. If supports are present, the same type of two-panel Mylar tent can be constructed as that for centrifugal pumps. In many instances, however, sufficiently large supports are not provided, or the distance between pump and driver is relatively long. In these cases, a cylindrical enclosure similar to that used for centrifugal pumps can be constructed. If it is impractical to extend the enclosure all the way from the pump seal to the pump driver, a seal can be made around the reciprocating shaft. This can usually be best made by using heavy aluminum foil and crimping it to fit closely around the shaft. The foil is attached to the Mylar plastic of the enclosure and sealed with duct tape.

If the temperature is too high or the potential points of contact are too numerous to insulate, an enclosure made of aluminum foil can be constructed. This enclosure is sealed around the pump and bearing housing using silicone fabric insulating tape, adjustable metal bands, or wire.

In cases where liquid and vapors are leaking from a pump, the enclosures described above for valves can be used. The outlet from the tent to the sampling train is placed at the top of the enclosure and as far away from spraying leaks as practical. Thus, entrainment of the liquid into the sampling train (and cold trap) is avoided. The rate of leakage of liquid is measured by collecting it over a measured length of time. A low point is formed in the tent to collect the liquid so its volume can be measured and converted to a mass rate. The total mass leak rate can then be estimated by adding the liquid mass leak rate to the gas mass leak rate.

4.3.3 Compressors

In general, the same types of tents that are suitable for pumps can be directly applied to compressors. The construction and application of these enclosures have been described in the preceding discussions of pump sampling and will not be repeated in this section.

Compressors generally handle light gases, and in many cases, the seals are enclosed. The seal enclosures are vented to the atmosphere at a high-point vent or may be vented to the blowdown/flare system.

If the seals are vented to a high-point vent, this vent line can be sampled. A Mylar bag can be constructed and sealed around the outlet of the

vent and connected to the sampling train. The leak rate from the vented compressor seals is then measured using the normal flow-through method.

If the high-point vents are inaccessible, the vent lines from the compressor seal enclosures can be disconnected at some convenient point between the compressor and the normal vent exit. Sampling is then done at this intermediate point.

When enclosed compressor seals are vented by means of induced draft blowers or fans, the outlet from the blower/fan can be sampled. In a previous study, a pitot tube was used to determine the air flow rate.[11] A sample of the outlet air was taken and returned to the laboratory for methane and nonmethane hydrocarbon analysis. Ambient air samples were taken around the compressor seal enclosure area at the same time and were analyzed for hydrocarbon content. The compressor seal leak rate was determined from the knowledge of air flow rate, its hydrocarbon content, and the hydrocarbon content of the ambient air.

4.3.4 Flanges

In most cases, the physical configurations of flanges lend themselves well to the determination of leak rates. For small to moderately large leaks from flanges with metal skin temperatures up to about 400°F, a narrow section of Mylar film can be used to span the open distance between the two flange faces of the leaking source. The Mylar is attached and sealed to each flange with duct tape. Connections (bulkhead fittings) for the water manometer and sampling train are attached to the Mylar.

When testing flanges with skin temperatures above 400°F, the outside perimeter of both sides of the flange connection are wrapped with asbestos insulating tape. Then, a narrow strip of aluminum foil can be used to span the opening between the flange faces. This narrow strip of material can be sealed against the asbestos tape using adjustable bands of stainless steel.

4.3.5 Relief Valves

Relief devices in gas/vapor service generally relieve to the atmosphere through a large diameter pipe which is normally located at a high point on the process unit that it serves. The "horns" can be easily bagged by placing a Mylar plastic bag over the opening and sealing it to the horn with duct tape. Because many of these devices are high above grade, accessibility to the

sampling train may be limited or prevented. It is sometimes possible to run a long piece of tubing from the outlet connection on the bag to the sampling train located at grade level or on a stable platform. And as discussed previously in the section on screening, the purpose of pressure relief devices makes them inherently dangerous to sample, especially over a long period of time. If these equipment are to be sampled for mass emissions, special care and precautions should be taken to ensure the safety of the personnel conducting the field sampling.

4.4 ACCURACY CHECKS

An accuracy check is normally performed in the laboratory by sampling an artificially induced leak rate of a known gas. This effectively points out any bias in the test methods and defines the variance component due to sampling. If the result is outside the 80 percent to 120 percent recovery range, the problem should be investigated and corrected before sampling continues. The problems and associated solutions should be noted in the test report.

4.5 ANALYTICAL TECHNIQUES

The techniques used in the laboratory analysis of the bagged samples will depend on the type of processes sampled. The following sections describe the analytical instrumentation, calibration, analytical techniques for condensate, and quality control. These are guidelines for the field sampling team and are not meant to be a detailed protocol for the laboratory personnel. Laboratory personnel should be well versed in the analysis of hydrocarbon mixtures and should design their specific analyses to the samples being examined.

4.5.1 Analytical Instrumentation

The selection of analytical instrumentation is critical to identification of individual organics in the sample. The instrument of choice depends on the type of sample being processed. Organic components of the streams of some process units may produce widely differing responses with an FID. For this reason, more comprehensive analyses by gas chromatography must be performed to identify individual components. FID gas chromatographs or electron capture gas chromatographs are commonly used to identify individual components of a sample. Other considerations besides instrument choice are the type of column used, and whether or not temperature programming is necessary to separate out

individual components of the process stream with sufficient resolution. An example of a gas chromatograph that has been used in previous studies is the Hewlett Packard 573-A Dual FID Gas Chromatograph.[12]

For some process streams such as ethylene and cumene, total hydrocarbon analyses are satisfactory. The response of the FID to these compounds is similar; therefore an instrument such as the Byron Total Hydrocarbon Analyzer (THC) can be calibrated with a single representative hydrocarbon. This instrument has an FID and resolves samples with methane and nonmethane components. The emission streams can then be analyzed for the total hydrocarbon content with reasonable accuracy.

4.5.2 Calibration

Proper calibration of both the laboratory and field instruments for the wide range of organic species is different. Each instrument must be calibrated with the appropriate species each day it is used.

Calibration of the portable hydrocarbon detector should be done with standards of hexane in air. A hexane standard of approximately 2,000 ppmv is available in a bottle supplied and certified to ± 2 percent by the manufacturer. Higher concentrations than this may lead to problems involving condensation at ambient temperatures. Lower concentrations must be generated by dilution.

The total hydrocarbon analyzer can be calibrated with the same hexane standard. The standard is related to an NBS propane standard by measuring the concentration of the NBS standard using the total hydrocarbon analyzer after the analyzer has been calibrated with the hexane standard.

The gas chromatograph is calibrated with either gas standards generated from calibrated permeation tubes containing individual VOC components or bottled standards of common gases.

4.5.3 Analytical Techniques for Condensate

Any condensate collected by the ice bath in the sampling train should be brought to the laboratory sealed in the cold trap flask. This material is transferred to a graduated cylinder to measure the volume collected. If there is enough volume to make it feasible, the organic layer should be separated from the aqueous layer (if present) and weighed to determine its density. Both the aqueous and organic phases should be analyzed by gas chromatography if water-miscible organic compounds are present.

4.5.4 Quality Control for Analytical Techniques

Blind standards should be prepared and submitted for analysis. The blind standards are prepared by diluting or mixing primary standards in a prescribed fashion so that the resulting concentrations are known. The calculated concentrations and the analytical results should be logged into a laboratory notebook. If the results are not within 25 percent of the certified level, further analyses must be performed to determine the reason. Such a procedure not only defines the analytical variance component and analytical accuracy, but it serves to point out equipment malfunctions and/or operator error before many data are affected.

SECTION 5.0
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APPENDIX A

REFERENCE METHOD 21

PROPERTY OF
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METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUNDS LEAKS

1. Applicability and Principle.

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

2. Definitions.

2.1 Leak Definition Concentration. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

2.2 Reference Compound. The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

2.3 Calibration Gas. The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

2.4 No Detectable Emission. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is not present. Since background VOC concentrations may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than a concentration corresponding to the minimum readability specification indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

2.5 Response Factor. The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

2.6 Calibration Precision. The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

2.7 Response Time. The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

3. Apparatus.

3.1 Monitoring Instrument.

3.1.1 Specifications.

a. The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

b. The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

c. The scale of the instrument meter shall be readable to ±5 percent of the specified leak definition concentration.

d. The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be ⅛ to 3 liters per minute.

e. The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association).

3.1.2 Performance Criteria.

a. The instrument response factors for the individual compounds to be measured must be less than 10.

b. The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

c. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

d. The evaluation procedure for each parameter is given in Section 4.4.

3.1.3 Performance Evaluation Requirements.

a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

3.2 Calibration Gases. The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, less than 10 ppmv VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration gas mixture are used, they must be analyzed and certified by the manufacturer to be within ±2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternately, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within ±2 percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results.

4. Procedures.

4.1 Pretest Preparations. Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

4.2 Calibration Procedures. Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE.—If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

4.3 Individual Source Surveys.

4.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

a. Valves—The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exists the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

b. Flanges and Other Connections—For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

c. Pumps and Compressors—Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

d. Pressure Relief Devices—The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

e. Process Drains—For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

f. Open-Ended Lines or Valves—Place the probe inlet at approximately the center of the opening to the atmosphere.

g. Seal System Degassing Vents and Accumulator Vents—Place the probe inlet at approximately the center of the opening to the atmosphere.

h. Access Door Seals—Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

4.3.2 Type II—"No Detectable Emission". Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration described in 4.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) Pump or Compressor Seals—If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices—If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in this paragraph shall be used to determine if detectable emissions exist.

4.3.3 Alternative Screening Procedure. A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument techniques of 4.3.1 or 4.3.2.

Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or a squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of 4.3.1 or 4.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

4.4 Instrument Evaluation Procedures. At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 Response Factor. Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 90 percent of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 90 percent of the saturation concentration, or 70 percent of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 5.

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and mutiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

5. Bibliography.

5.1 DuBose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-061. September 1981.

5.2 Brown, G.E., et al. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-022. May 1981.

5.3 DuBose, D.A., et al. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-110. September 1981.

APPENDIX B

RESPONSE FACTORS

This appendix presents response factors estimated for a 10,000 ppmv detector reading. These response factors were previously reported in References 4 and 6. They can be used to determine whether or not a concentration is above or below 10,000 ppmv. The response factors may or may not be accurate at other concentrations.

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE

CAS No.*	Compound Name	Volatility Class	OVA				TLV			
			Response Factor		Confidence Intervals		Response Factor		Confidence Intervals	
64-19-7	Acetic acid	LL	1.64		1.11,	2.65	15.60		7.05,	46.20
108-24-7	Acetic anhydride	LL	1.39		1.09,	1.86	5.88	I	2.71,	12.80
67-64-1	Acetone	LL	0.80		0.57,	1.20	1.22		0.81,	2.00
75-86-5	Acetone cyanohydrin	HL	3.51		0.69,	>100.00	21.00	N	1.09,	>100.00
75-05-8	Acetonitrile	LL	0.95		0.85,	1.06	1.18		0.94,	1.52
98-86-2	Acetophenone	HL	18.70		5.52,	>100.00		B		
75-36-5	Acetyl chloride	LL	2.04		1.72,	2.48	2.72		1.65,	5.32
74-86-2	Acetylene	G	0.39		0.36,	0.43		B		
79-10-7	Acrylic acid	LL	4.59		3.38,	6.57		B		
107-13-1	Acrylonitrile	LL	0.97		0.80,	1.20	3.49	I	0.44,	27.90
	Allene	G	0.64		0.60,	0.69	15.00		9.68,	26.50
107-18-6	Allyl alcohol	LL	0.96		0.76,	1.27		X		
71-41-0c	Amyl alcohol, N-	HL	0.75		0.57,	1.04	2.14		0.45,	>100.00
	Amylene	LL	0.44		0.34,	0.61	1.03		0.59,	2.59
100-66-3	Anisole	LL	0.92		0.65,	1.46	3.91		0.52,	>100.00
100-52-7	Benzaldehyde	HL	2.46		1.38,	5.62		B		
71-43-2	Benzene	LL	0.29		0.28,	0.31	1.07		0.96,	1.20
100-47-0	Benzonitrile	HL	2.99		1.18,	15.30		B		
98-88-4	Benzoyl chloride	HL	22.10	D	3.43,	>100.00		B		
100-44-7	Benzyl chloride	HL	15.30	D	3.96,	>100.00		B		
10-86-1	Bromobenzene	L	0.40		0.34,	0.48	1.19		0.27,	>100.00
106-99-0	Butadiene, 1,3-	G	0.57		0.54,	0.60	10.90		8.11,	15.40
	Butane, N-	G	0.50		0.46,	0.55	0.63		0.58,	0.70
	Butanol, N-	LL	1.44	I	0.89,	2.34	4.11	I	2.16,	7.83
	Butanol, Sec-	LL	0.76		0.70,	0.83	1.25		0.99,	1.66
	Butanol, Tert-	S	0.53		0.38,	0.81	2.17		1.34,	4.43
106-98-9	Butene, 1-	G	0.56		0.51,	0.62	5.84		4.20,	8.89
123-86-4	Butyl acetate	LL	0.66		0.54,	0.83	1.38		1.15,	1.70
141-32-2	Butyl acrylate, N-	LL	0.70		0.63,	0.78	2.57	I	1.17,	5.68
	Butyl ether, N-	LL	2.60		0.81,	95.60	3.58	I	1.82,	7.04
	Butyl ether, Sec-	LL	0.35		0.21,	0.95	1.15		0.75,	2.17

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA Response Factor		OVA Confidence Intervals		TLV Response Factor		TLV Confidence Intervals	
109-73-9	Butylamine, N-	LL	0.69		0.53,	0.98	2.02		1.14,	4.97
13952-84-6	Butylamine, Sec-	LL	0.70		0.58,	0.87	1.56		0.77,	5.24
75-64-9	Butylamine, Tert-	LL	0.63		0.58,	0.70	1.95		1.42,	2.91
	Butylbenzene, Tert-	HL	1.32		0.89,	2.20		B		
123-72-8	Butyraldehyde, N-	LL	1.29		1.07,	1.61	2.30		0.96,	12.80
107-92-6	Butyric acid	HL	0.80		0.38,	3.14	10.70	I	6.53,	17.60
109-74-0	Butyronitrile	LL	0.52		0.40,	0.74	1.47	I	0.62,	3.48
75-1-50	Carbon disulfide	LL		B			3.92		1.87,	12.60
	Chloroacetaldehyde	LL	9.10		5.73,	16.20	5.07		3.08,	9.79
108-90-7	Chlorobenzene	LL	0.38		0.32,	0.47	0.88		0.77,	1.00
	Chloroethane	G	5.38	I	1.87,	26.40	3.90	P	1.58,	14.10
67-66-3	Chloroform	L	9.28		5.19,	20.00		B		
25167-80-0	Chlorophenol, O-	HL	4.56		1.72,	27.20	18.30	I	6.50,	51.50
	Chloropropene, 1-	LL	0.67		0.61,	0.73	0.87		0.69,	1.16
	Chloropropene, 3-	LL	0.80		0.72,	0.90	1.24		1.08,	1.42
108-41-8	Chlorotoluene, M-	LL	0.48		0.45,	0.51	0.91		0.40,	7.47
95-49-8	Chlorotoluene, O-	LL	0.48		0.42,	0.55	1.06		0.33,	>100.00
106-43-4	Chlorotoluene, P-	LL	0.56		0.52,	0.61	1.17	I	0.77,	1.77
95-48-7	Cresol, O-	S	0.96		0.70,	1.45	4.36	I	0.40,	47.40
4170-30-0	Crotonaldehyde	LL	1.25		0.82,	2.24		B		
98-82-8	Cumene	LL	1.87		1.10,	3.71		B		
110-82-7	Cyclohexane	LL	0.47		0.39,	0.58	0.70		0.62,	0.80
108-93-0	Cyclohexanol	HL	0.85		0.65,	1.20		B		
108-94-1	Cyclohexanone	LL	1.50		0.97,	2.76	7.04		1.59,	>100.00
110-83-8	Cyclohexene	LL	0.49		0.42,	0.57	2.17		1.78,	2.74
108-91-8	Cyclohexylamine	LL	0.57		0.42,	0.86	1.38		1.28,	1.48
	Decane	HL	0.09	N	0.05,	>100.00	0.16	I	0.07,	0.35
123-42-2	Diacetone alcohol	HL	1.45		0.96,	2.48	0.98		0.44,	5.93
	Diacetyl	LL	1.54		1.25,	1.92	3.28		2.25,	5.12
	Dichloro-1-propene, 2,3-	LL	0.75		0.56,	1.09	1.75		1.14,	3.18

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA			TLV			
			Response Factor		Confidence Intervals	Response Factor		Confidence Intervals	
541-73-1	Dichlorobenzene, M-	HL	0.64		0.55, 0.77	2.36		0.58,	>100.00
95-50-1	Dichlorobenzene, O-	HL	0.68		0.47, 1.11	1.26		0.35,	>100.00
	Dichloroethane, 1,1-	LL	0.78		0.62, 1.02	1.86		1.56,	2.25
107-06-2	Dichloroethane, 1,2-	LL	0.95		0.77, 1.22	2.15		1.66,	2.92
	Dichloroethylene, CIS1,2-	LL	1.27		1.05, 1.56	1.63		0.99,	3.47
	Dichloroethylene, TRANS 1,2-	LL	1.11		0.98, 1.27	1.66		0.67,	12.60
	Dichloromethane	LL	2.81		2.13, 3.87	3.85		2.46,	6.88
	Dichloropropane, 1,2-	LL	1.03		0.82, 1.33	1.65		1.06,	3.05
25167-70-8	Diisobutylene	LL	0.35		0.29, 0.44	1.41		0.96,	2.40
	Dimethoxy ethane, 1,2-	LL	1.22		0.64, 3.61	1.52		0.65,	8.38
68-12-2	Dimethylformamide, N,N-	LL	4.19		2.90, 6.58	5.29		4.05,	7.20
57-14-7	Dimethylhydrazine, 1,1-	LL	1.03		0.77, 1.45	2.70		0.51,	>100.00
67-68-5	Dimethylsulfoxide	HL	0.07	I	0.05, 0.11	8.45	I	4.15,	17.20
123-91-1	Dioxane	LL	1.48		1.04, 2.33	1.31		0.70,	3.60
106-89-8	Epichlorohydrin	LL	1.69		1.56, 1.84	2.03		1.79,	2.33
	Ethane	G	0.65		0.44, 1.58	0.69	I	0.21,	2.30
64-17-5	Ethanol	LL	1.78		1.59, 2.01		X		
	Ethoxy ethanol, 2-	LL	1.55		1.26, 1.96	1.82		0.96,	5.12
141-78-6	Ethyl acetate	LL	0.86		0.77, 0.95	1.43		1.07,	2.00
141-97-9	Ethyl acetoacetate	HL	3.82		1.89, 10.70	5.60		1.93,	38.80
140-88-5	Ethyl acrylate	LL	0.77		0.63, 0.97		X		
105-39-5	Ethyl chloroacetate	LL	1.99		1.70, 2.36	1.59		0.40,	>100.00
	Ethyl ether	LL	0.97		0.77, 1.30	1.14		0.94,	1.42
100-41-4	Ethylbenzene	LL	0.75		0.52, 1.11	4.74	D	1.38,	61.30
74-85-1	Ethylene	G	0.71		0.63, 0.82	1.56		1.26,	2.06
75-21-8	Ethylene oxide	G	2.46		1.95, 3.29	2.40		0.96,	>100.00
107-15-3	Ethylenediamine	LL	1.73		1.29, 2.46	3.26		0.78,	>100.00
64-18-6	Formic acid	LL	14.20		10.60, 19.80		B		
	Glycidol	LL	6.88		3.33, 19.70	5.66		2.08,	34.70

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA Response Factor		OVA Confidence Intervals		TLV Response Factor		TLV Confidence Intervals	
	Heptane	LL	0.41	I	0.28,	0.60	0.73		0.33,	6.10
	Hexane, N-	LL	0.41		0.38,	0.45	0.69		0.63,	0.76
	Hexene, 1-	LL	0.49		0.39,	0.66	4.69	D	0.85,	>100.00
	Hydroxyacetone	LL	6.90		4.45,	12.10	15.20		6.11,	66.40
	Isobutane	G	0.41		0.29,	1.04	0.55		0.41,	0.81
115-11-7	Isobutylene	G	3.13		0.90,	38.50		B		
78-79-5	Isoprene	LL	0.59		0.46,	0.80		X		
67-63-0	Isopropanol	LL	0.91		0.72,	1.20	1.39		0.94,	2.31
108-21-4	Isopropyl acetate	LL	0.71		0.62,	0.83	1.31		1.04,	1.72
75-29-6	Isopropyl chloride	LL	0.68		0.60,	0.77	0.98		0.82,	1.22
	Isovaleraldehyde	LL	0.64		0.57,	0.74	2.19	D	1.14,	6.65
141-79-7	Mesityl oxide	LL	1.09		0.94,	1.29	3.14		1.43,	12.00
	Methacrolein	LL	1.20		0.90,	1.71	3.49	D	1.51,	19.80
79-41-4	Methacrylic acid	HL	0.82		0.31,	14.70	1.06	I	0.24,	4.56
67-56-1	Methanol	LL	4.39	P	3.61,	5.60	2.01		1.66,	2.48
	Methoxy-ethanol, 2-	LL	2.25		1.62,	3.34	3.13		1.13,	27.40
79-20-9	Methyl acentate	LL	1.74		1.46,	2.13	1.85		1.44,	2.49
	Methyl acetylene	G	0.61		0.58,	0.64	6.79		4.86,	10.40
74-87-3	Methyl chloride	G	1.44		1.22,	1.76	1.84		0.73,	>100.00
78-93-3	Methyl ethyl ketone	LL	0.64		0.51,	0.84	1.12		0.93,	1.38
107-31-3	Methyl formate	LL	3.11		2.42,	4.14	1.94		1.72,	2.21
80-62-6	Methyl methacrylate	LL	0.99		0.90,	1.10	2.42		1.39,	5.38
	Methyl-2-pentanol, 4-	LL	1.66		1.27,	2.32	2.00		1.40,	3.15
	Methyl-2-pentanone, 4-	LL	0.56		0.46,	0.69	1.63		1.22,	2.35
	Methyl-3-butyn-2-OL, 2-	LL	0.59		0.44,	0.86		X		
	Methylal	LL	1.37		1.06,	1.83	1.46		1.24,	1.74
100-61-8	Methylaniline, N-	HL	4.64		3.91,	5.57	9.46		2.55,	35.20
108-87-2	Methylcyclohexane	LL	0.48		0.28,	1.39	0.84		0.68,	1.09
	Methylcyclohexene, 1-	LL	0.44		0.36,	0.54	2.79		1.79,	5.12

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA				TLV			
			Response Factor		Confidence Intervals		Response Factor		Confidence Intervals	
77-75-8	Methylpentynol	LL	1.17		0.71,	2.48	3.42		1.83,	8.54
98-83-9	Methylstyrene, A-	LL	13.90		9.50,	21.50		B		
110-91-8	Morpholine	LL	0.92		0.67,	1.40	2.59	I	0.64,	10.50
98-95-3	Nitrobenzene	HL		B			0.01	I	0.00,	82.80
79-24-3	Nitroethane	LL	1.40		1.20,	1.65	3.45		1.56,	13.00
75-52-5	Nitromethane	LL	3.52		3.03,	4.15	7.60		1.91,	>100.00
25332-01-4	Nitropropane	LL	1.05		0.80,	1.48	2.02		1.17,	4.47
	Nonane-N	LL	1.54		0.94,	2.98	11.10		3.13,	>100.00
	Octane	LL	1.03		0.89,	1.21	2.11		1.68,	2.75
109-66-0	Pentane	LL	0.52		0.42,	0.66	0.63		0.57,	0.70
	Picoline, 2-	LL	0.43		0.38,	0.50	1.18		1.08,	1.29
	Propane	G	0.55	I	0.46,	0.72	0.60	P	0.59,	0.69
123-38-6	Propionaldehyde	LL	1.14		1.00,	1.32	1.71		1.11,	3.06
79-09-4	Propionic acid	LL	1.30		1.03,	1.70	5.08	D	0.73,	>100.00
71-23-8	Propyl alcohol	LL	0.93		0.77,	1.16	1.74		1.06,	3.50
	Propylbenzene, N-	LL	0.51		0.45,	0.58		B		
115-07-1	Propylene	G	0.77		0.44,	2.66	1.74	I	0.15,	20.30
75-56-9	Propylene oxide	LL	0.83		0.74,	0.95	1.15		0.69,	2.46
110-86-1	Pyridine	LL	0.47		0.40,	0.55	1.16		1.03,	1.34
100-42-5	Styrene	LL	4.22		3.45,	5.27		B		
79-34-5c	Tetrachloroethane, 1,1,1,2-	LL	4.83	D	1.24,	>100.00	6.91		3.14,	22.50
	Tetrachloroethane, 1,1,2,2-	LL	7.89		5.01,	13.80	25.40		8.06,	>100.00
	Tetrachloroethylene	LL	2.97		1.71,	6.11		B		
108-88-3	Toluene	LL	0.39		0.36,	0.43	2.68	D	0.79,	>100.00
	Trichlorobenzene, 1,2,4-	HL	1.21	I	0.50,	2.94	0.47	I	0.32,	0.68
71-55-6	Trichloroethane, 1,1,1-	LL	0.80		0.72,	0.90	2.40		1.81,	3.35
79-00-5	Trichloroethane, 1,1,2-	LL	1.25		1.05,	1.50	3.69		2.77,	5.16
79-01-6	Trichloroethylene	LL	0.95		0.83,	1.09	3.93		2.68,	6.32
96-18-4	Trichloropropane, 1,2,3-	LL	0.96		0.64,	1.78	1.99		1.27,	3.82

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA Response Factor		OVA Confidence Intervals		TLV Response Factor		TLV Confidence Intervals	
121-44-8	Triethylamine	LL	0.51		0.40,	0.70	1.48		0.96,	2.76
108-05-4	Vinyl acetate	LL	1.27		0.95,	1.82	5.91	D	1.26,	>100.00
75-01-4	Vinyl chloride	G	0.84		0.61,	1.38	1.06		0.59,	4.60
	Vinyl propionate	LL	1.00	I	0.57,	1.74	1.21	I	0.46,	3.20
75-35-4	Vinylidene chloride	LL	1.12		0.87,	1.52	2.41		1.82,	3.35
106-42-3	Xylene, P-	LL	2.12		1.71,	2.68	7.87		3.49,	24.90
	Xylene, M-	LL	0.40		0.36,	0.46	5.87	D	0.91,	>100.00
95-47-6	Xylene, O-	LL	0.43		0.28,	0.85	1.40		0.61,	9.33

*CAS numbers refer to the Chemical Abstracts Registry numbers of specific chemicals, isomers, or mixtures of chemicals.

G = Gas; LL = light liquid; HL = heavy liquid

I = inverse estimation method

D = possible outliers in data

N = narrow range of data

X = no data available

B = 10,000 ppmv response unachievable

P = suspect points eliminated

TABLE B-2. TESTED COMPOUNDS WHICH APPEAR TO BE UNABLE TO ACHIEVE AN INSTRUMENT RESPONSE OF 10,000 PPMV AT ANY FEASIBLE CONCENTRATION

Instrument[a]	OVA		TLV
CAS[b]	Compound Name	CAS[b]	Compound Name
--	Acetyl-1-propanol, 3-	98-86-2	Acetophenone
75-1-50	Carbon disulfide	--	Acetyl-1-propanol, 3-
56-23-5	Carbon tetrachloride	74-86-2	Acetylene
--	Dichloro-1-propanol, 2,3	79-10-7	Acrylic acid
--	Dichloro-2-propanol, 1,3	100-52-7	Benzaldehyde
--	Diisopropyl benzene, 1,3	100-47-0	Benzonitrile
--	Dimethylstyrene, 2,4	98-88-4	Benzoyl chloride
1221	Freon 12	100-44-7	Benzyl chloride
98-01-1	Furfural	--	Butylbenzene, Tert-
--	Methyl-2,4-pentanediol,2	56-23-5	Carbon tetrachloride
1660	Monoethanolamine	67-66-3	Chloroform
98-95-3	Nitrobenzene	4170-30-0	Crotonaldehyde
108-95-2	Phenol	98-82-8	Cumene
--	Phenyl-2-propanol, 2-	108-93-0	Cyclohexanol
		--	Dichloro-1-propanol, 2,3
		--	Dichloro-2-propanol, 1,3
		--	Diisopropyl benzene, 2,4
		--	Dimethylstyrene, 2,4
		64-18-6	Formic acid
		1221	Freon 12
		98-01-1	Furfural
		115-11-7	Isobutylene
		--	Methyl-2,4-pentanediol
		98-83-9	Methylstyrene, A-
		1660	Monoethanolamine
		108-95-2	Phenol
		--	Phenyl-2-propanol, 2-
		--	Propylbenzene, N-
		100-42-05	Styrene
		2860	Tetrachloroethylene

[a]OVA and TLV are two portable hydrocarbon analyzers that have been used in previous studies of fugitive emissions. Operating with a flame ionization detector (FID), OVA measures nonmethane hydrocarbon emissions; TLV measures total hydrocarbon emissions.

[b]CAS numbers refer to the Chemical Abstracts Registry numbers of specific chemicals, isomers, or mixtures of chemicals.

APPENDIX C

CALCULATION OF MASS EMISSION RATES

APPENDIX C

The calculation of emission rates is illustrated below for VOC:

$$E_T = E_V + E_L$$

where E_T = total VOC emission rate, lb/hr,

E_L = condensed organic liquid component of the VOC emission rate, lb/hr, and

E_V = vapor component of the VOC emission rate, lb/hr.

The emission rate of the vapor component is calculated from the following equation:

$$E_V = K \frac{QPM_A (C_s - C_a)}{T}$$

where K = 5.6×10^{-6}, a factor incorporating conversion factors and standard temperature and pressure,

Q = flow rate of gas through the sample train, actual cubic feet/minute,

P = sampling system pressure at the dry gas meter, psia,

M_A = molecular weight of the air/VOC mixture,

C_s = concentration of VOC in the gas sample from the sampling train, ppm by weight,

C_a = concentration of VOC in the ambient air, ppm by weight, and

T = sampling system temperature at the dry gas meter, ^{o}R.

The emission rate of the organic condensate component, E_L, is determined from the following equation:

$$E_L = \frac{0.1\ V}{t}$$

where E_L = organic condensate rate, lb/hr,

V = volume of condensate collected, ml, and

t = time over which the sample was collected, min.

This calculation assumes an average density of 0.75 g/cc for the organic condensate.

These equations can be modified as necessary to provide for water-miscible compounds and to express emissions in terms of compounds other than hexane.

APPENDIX D

LEAK RATE/SCREENING VALUE EQUATIONS

TABLE D-1. PREDICTION EQUATIONS FOR NONMETHANE LEAK RATE FOR VALVES, FLANGES, AND PUMP SEALS IN SOCMI PROCESSES

SOURCE TYPE	INSTRUMENT	LEAST - SQUARES EQUATION[c]	NUMBER OF DATA PAIRS	CORRELATION COEFFICIENT (r)	STANDARD DEVIATION OF ESTIMATE
Valves[a]					
Gas Service	OVA	$NMLK = 1.68\ (10^{-5})\ (MXOVA)^{0.693}$	99	0.66	0.716
Light Liquid Service	OVA	$NMLK = 3.74\ (10^{-4})\ (MXOVA)^{0.47}$	129	0.47	0.902
Flanges[b]	OVA	$NMLK = 3.731\ (10^{-5})\ (MXOVA)^{0.82}$	52	0.77	0.520
Pump Seals[a]	OVA	$NMLK = 1.335\ (10^{-5})\ (MXOVA)^{0.898}$	52	0.81	0.650

NMLK = Nonmethane leak rate (lb/hr)
MXOVA = Maximum screening value (ppmv) - OVA instrument

[a]Source: Langley, G. J., and R. G. Wetherold (Radian Corporation) 1981. Evaluation of Maintenance for Fugitive VOC Emissions Control. EPA-600/52-81-080. pp. 54-56.

[b]Source: Wetherold, R.G., L.P. Provost, and C.D. Smith (Radian Corporation). Assessment of Atmospheric Emissions from Petroleum Refining: Volume 3. Appendix B. (Prepared for U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina. Publication No. EPA-600/2-80-075c.

[c]NMLK is given in units of lb/hr. The units may have to be changed for reporting purposes.

APPENDIX E

SELECTION OF SAMPLE SIZE FOR FLANGE SCREENING

APPENDIX E

SELECTION OF SAMPLE SIZE FOR SCREENING FLANGES AND OTHER CONNECTORS

In estimating emissions for a given process unit, all equipment components must be surveyed for each class of components. For example, all valves in gas/vapor service must be screened to establish the number of components in each of the given ranges of screening values. The one exception to this "total component screening" criterion is the category of flanges and other connectors. In typical process units, flanges and other connectors represent the largest count of individual equipment components, making it costly to screen all components. The purpose of this appendix is to present a methodology for determining how many flanges or other connectors must be screened to constitute a large enough sample size to identify the actual screening value distribution of flanges and other connectors in the entire process unit. Please note that the sampling is to be a random sampling throughout the process unit.

The basis for selecting the sample population to be screened is the probability that at least one "leaking" flange will be in the screened population. The "leaker" is used as a representation of the complete distribution of screening values for the entire class of sources. The following binomial distribution was developed to approximate the number of flanges and other connectors that must be screened to ensure that the entire distribution of screening values for these components is represented in the sample:

$$n \geq N * [1 - (1 - p)^{1/D}] \qquad \text{(E-1)}$$

where D may be taken as (fraction of leaking flanges) * N and $p \geq 0.95$.

Currently available data gathered for flanges in VOC service in chemical process units show an estimated 2.09 percent flanges leaking. The EPA recommends starting with the factor 0.0209 for the fraction of leaking flanges, since the actual leak frequency for flanges in a chemical process unit probably will not be known prior to the selection of a sample size for screening. A larger sample size will be required for units exhibiting a lower fraction of leaking flanges and other connectors. If a lower leak frequency

for a process unit is known or can be estimated, it may be substituted into the equation above in place of 0.0209.

After 'n' flanges have been screened, an actual leak frequency should be calculated as follows:

$$\text{Leaking Frequency} = \frac{\text{Number of leaking flanges}}{n} \qquad \text{(E-2)}$$

Then, the confidence level of the sample size can be calculated using the following equation, based upon a hypergeometric distribution:

$$P = 1 - \frac{(N-D')!\ (N-n)!}{N!\ (N-D'-n)!} \qquad \text{(E-3)}$$

where N = Total population of flanges and other connectors

n = Sample size

$$D' = \frac{\text{Number of leaking flanges and connectors}}{n} * N$$

If 'p' calculated in this manner is less than 0.95, then a less than 95 percent confidence exists that the screening value distribution has been properly identified. Therefore, additional flanges/connectors must be screened to achieve a 95 percent confidence level. The number of additional flanges required to satisfy the requirement for a 95 percent confidence level can be calculated by solving Equation (E-1) again, using the leak frequency calculated in Equation (E-2), and subtracting the original sample size. After this additional number of flanges/connectors have been screened, the revised fraction of leaking components and the confidence level of the new sample size (i.e., the original sample size plus the additional flanges/connectors screened) should be recalculated using Equation (E-3). The Agency requires sufficient screening to achieve a 95 percent confidence level, until a maximum of 50 percent of the total number of flanges and other connectors in the process unit have been screened. The EPA believes that 50 percent of the total flange/connector population is a reasonable upper limit for a sample size. If half of the total number of flanges and other connectors are screened, no further flange screening is necessary, even if a 95 percent confidence level has not been achieved.

APPENDIX F

DETERMINATION OF EMISSION RATES FOR DEFAULT ZERO SCREENING VALUES

APPENDIX F

DETERMINATION OF EMISSION RATES FOR DEFAULT ZERO SCREENING VALUES

In developing emission estimates using correlations, the emissions associated with zero screening values are estimated using default emission rates. Due to their logarithmic form, the correlations estimate zero emissions for zero screening values. Field testing, however, indicates that there are finite emissions associated with equipment screening at the background concentrations. To account for these emissions in the protocol, EPA has established some default zero screening values and their associated emission rates based on data gathered during the SOCMI Maintenance Study.

Twelve data pairs for valves in gas/vapor service were bagged to determine mass emissions during the Maintenance Study. The mass emission rates for these twelve sources were averaged to establish the emission rate for gas/vapor valves screening at 0 ppm above the background level. This average emission rate is 0.000033 kilograms per hour per source. Using the SOCMI/OVA correlation for gas/vapor valves shown in Appendix D and this emission rate, the "default zero" screening value was established (8 ppm). All components screening at or below this default screening value are assumed to have an emission rate equal to the default zero emission rate.

No mass emissions data for zero screening values were available for equipment components other than valves in gas/vapor service. The default zero emission rates for all equipment types and services were established using the correlations shown in Appendix D and the default zero screening value (8 ppm) calculated from the gas/vapor valves bagging data.

Equipment Type/Service	"Default Zero" Screening Value, ppm	Zero Screening Value Emission Rate (kg/hr/source)
Valves, gas	8	0.000033
Valves, light liquid	8	0.000451
Flanges	8	0.000093
Pumps and all other components	8	0.000039

APPENDIX G

DEVELOPMENT OF A DEFAULT EMISSION RATE FOR EQUIPMENT THAT DOES NOT SCREEN ABOVE THE BACKGROUND CONCENTRATION

Text adapted from Guidance for Estimating Fugitive Emissions, published by the Chemical Manufacturers Association.

The average, standard deviation, and scale bias correction factor (SBCF) are calculated for the Y_i as follows:

$$\bar{y} = \frac{1}{n} \sum_{i=1}^{n} y_i$$

$$S^2 = \frac{1}{n-1} \sum_{i=1}^{n} (y_i - \bar{y})^2$$

$$SBCF = g\,[(\ln 10)^2\,(S^2/2)]$$

where $g(t) = 1 + \frac{(n-1)}{n}\,t + \frac{(n-1)^3 t^2}{n^2 2!(n+1)} + \frac{(n-1)^5 t^3}{n^3 3!(n+1)(n+3)} + \ldots$

(Approx. 10-15 terms required to obtain accuracy of $+ 10^{-7}$)

The estimate of emissions for components screening below the lower limit of detection (LLD) for the screening instrument, (EF_{1*}), is then:

$$EF_1{}^* = \max\,[(10^{\bar{y}} SBCF) - C,\ \emptyset]$$

where $C = \emptyset$ for Case 1, and previously stated for Case 2 and Case 3.

A statistical test is used to compare the calculated EF_{1*} with the established 'default zero' in Appendix F. The results of this test determine which value (EF_{1*} or 'default zero') is used to represent emissions for components screening below the LLD. The test involves two cases:

APPENDIX G

DEVELOPMENT OF A DEFAULT EMISSION RATE FOR EQUIPMENT THAT DOES NOT SCREEN ABOVE THE BACKGROUND CONCENTRATION.

If bagging data for equipment components that do not screen above background do not exist, the EPA default emission rates in Appendix F should be used to estimate emissions from these sources. If a process unit intends to develop its own default zero emission rates, it must bag samples from each equipment type (e.g., gas/vapor valves, light liquid valves) for which it plans to determine default zero emission rates. If bagging data exist, the first step in developing a default emission rate is to adjust for the background concentration by subtracting the background bag from the source bag; that is, calculate

$$X_i = LR_{S,i} - LR_{B,i}$$

where $LR_{S,i}$ = leak rate from source bag i

$LR_{B,i}$ = leak rate from background bag i

Next, take the logarithm of the data and add a constant (if necessary) to avoid taking the logarithm of a nonpositive X_i. The following procedure is used:

Case 1: If all of the data are positive, $y_i = \log(Xi)$

Case 2: If all of the data are nonnegative with at least one zero,

$$y_i = \log(Xi + C)$$

where C = largest power of 10 less than the smallest nonzero value of X (e.g., if the smallest nonzero value of X is 8×10^{-4}, then $C = 1 \times 10^{-4}$).

Case 3: If some of the data are negative, the smallest value (K1) is first subtracted from each observation in the data set (note that K1 is a negative number). This results in all nonnegatives, with at least one zero value. Then K2 is added to each observation in the set, where K2 = largest power of 10 less than the smallest nonzero value of the updated nonnegative data set. Hence, the logarithmic expression used is

$$y_i = \log(Xi + C) \quad \text{where } C = K2\text{-}K1$$

Case A: If EF_{1*}<'Default zero', then use EF_{1*} if

$$EF_{UL} = 10^{\bar{y}+t(.95,\ n-1)\sqrt{S^2/n}} \qquad \text{SBCF} < \text{'Default zero'}$$

(Use 'Default zero' if $EF_{UL} \geq$ 'Default zero')

Case B: If EF_{1*} > 'Default zero', then use EF_{1*} if

$$EF_{LL} = 10^{\bar{y}-t(.95,\ n-1)\sqrt{S^2/n}} \qquad \text{SBCF} > \text{'Default zero'}$$

(Use 'Default zero' if $EF_{LL} \leq$ 'Default zero')

A confidence interval for EF_1 can be calculated as:

$$(10^{\bar{y}+t_1(.975,\ n-1)\sqrt{S^2/n}} \text{ SBCF},\ 10^{\bar{y}+t_1(.975,\ n-1)\sqrt{S^2/n}} \text{ SBCF})$$

Note: This interval should only involve the nonnegative region. In the case where the above computation includes negative values, it should be truncated to zero.

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT
EPA has developed a Protocol for Generating Unit-Specific Emission Estimates fir Equipment Leaks of VOC and VHAP. The protocol provides several methods for estimating emissions from equipment leaks. These methods range from the application of average emission factors for the equipment component inventory to the use of bagging data for generating unit-specific leak rate/screening value correlations. In addition, the protocol provides technically sound methods of source screening and mass emissions sampling (bagging). The document will help facitilies generate accurate plant-specific equipment leak emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Petroleum Refinery Enforcement Manual

SECTION 5

ENFORCEMENT PROCEDURES

Each petroleum refinery is designed, engineered, constructed, and operated to process specific crude oils and produce specific products. This results in each petroleum refinery being unique in the complexity and number of processes employed. Since there is no typical refinery, a standard procedure for conducting the inspection does not exist. This section describes approaches to conducting an inspection rather than describing a standard procedure for the inspector to follow.

5.1 INTRODUCTION

This section describes the various levels of enforcement inspections and lists the process units and other emission sources that are to be inspected on those levels.

A thorough search should be conducted of the file for the refinery to be inspected to determine what process units are there, to note compliance history and trends, and to collect other pertinent data. The inspection checklists (which are given in Appendixes J through M) should be filled out as much as possible from file data. The data can then be verified and additional data collected during the inspection. The checklists are merely a means of organizing data; they are not official forms.

The inspector should be as informed as possible before entering the refinery, and one way to accomplish this is to review the descriptions of the various refining processes (Section 4). The inspector should review the subsections pertaining to those units that will be inspected. Appendix B and Appendix C

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provide additional background on the chemical engineering principles applicable to petroleum refining. The more an inspector knows about an industry he is inspecting, the better he will be able to communicate with plant personnel and the better the inspection will be. The inspector is cautioned not to appear to possess more knowledge of a subject than he actually has; by doing so, he may miss getting important information or discredit himself if plant personnel detect an area of ignorance. An honest, questioning approach is generally the most effective.

It is important that the inspector be assertive in order to assess compliance. The inspector should guide the course of the inspection and be persistent in getting and verifying important data. For example, the inspector may have a list of process units and their feed rates. Rather than accepting the word of the plant personnel aiding in the inspection, the inspector should ask to see production sheets or a logbook that will verify these data. An inspector should be confident that correct data are collected. This approach, although time consuming, is effective in uncovering additional compliance problems.

The following subsections describe three levels of inspection, which increase in degree of intensity and follow different time schedules. The Level I inspection is aimed at obtaining continuing compliance of a limited number of units. These units are the most likely to cause emission problems. The purpose of a Level II inspection is to obtain compliance with particulate, sulfur oxide, nitrous oxide, and some hydrocarbon emission regulations. In a Level II inspection more units are investigated than on a Level I inspection. The Level III inspection is aimed at obtaining strict compliance with hydrocarbon emission regulations. The number of fugitive emission sources monitored on a Level III inspection is much greater than the number monitored on a Level II inspection. Level II and III inspections are similar in the number of sources investigated for compliance with particulate, sulfur oxide, and nitrous oxide emission regulations. In the future, a fourth or very detailed inspection may be added.

This manual does not rule out that possibility, which would result from new state and Federal policies.

5.2 LEVEL I INSPECTION

It is recommended that a Level I inspection be performed once every 2 to 4 months. The actual frequency depends on the workload and manpower available at local, state and Federal offices. The duration of the inspection depends on the size of the refinery and the number of inspectors. A two-man inspection team can investigate a 30,000 barrel per day refinery in 2 to 3 hours.

Note the overall condition of the refinery during this inspection. Dust from the unpaved roads is a source of particulate emissions, and pools of oily water are a source of hydrocarbon emissions. Observe all heater and boiler stacks to monitor opacity. When a heater or a boiler stack is out of compliance with the state visible emission standard, complete the the visible emission observation form. (This form is illustrated here in Figure 5-1.)

Review and investigate the following units:

Unit	Pollutant
Fluid catalytic cracking	Particulates; sulfur dioxide
Sulfur recovery	Sulfur dioxide

The pollution control equipment that may be present at the Fluid Catalytic Cracking (FCC) unit includes a CO boiler, an electrostatic precipitator (ESP), and internal and external cyclones. Note the type of control equipment that is used and also note whether the CO boiler or ESP is bypassed during the inspection. (A refinery that does not have a flare, bypasses the CO boiler to the FCC sump stack.)

Sulfur dioxide emissions from a sulfur plant are continuously monitored at incinerator stacks by recording the incinerator temperature. The usual incinerator temperature is about

VISIBLE EMISSION OBSERVATION FORM

SOURCE NAME_____ OBSERVER_____

ADDRESS_____ DATE_____

Point of Emission_____

OBSERVATION POINT_____

STACK: DISTANCE FROM____ HEIGHT____

WIND-SPEED_____ DIRECTION_____

SKY CONDITION:_____

COLOR OF EMISSION:_____

RELATIVE HUMIDITY:_____

BACKGROUND:_____

AMBIENT AIR TEMPERATURE:_____

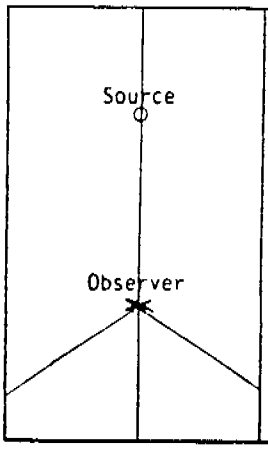
_____

CERTIFICATION DATE:_____

SUMMARY OF AVERAGE OPACITY

Set Number	Time Start--End	Opacity Sum	Opacity Average

Observer ×
Sun ☼ Wind ⟶ Plume & Stack



Remarks:

	0	15	30	45		0	15	30	45
0					30				
1					31				
2					32				
3					33				
4					34				
5					35				
6					36				
7					37				
8					38				
9					39				
10					40				
11					41				
12					42				
13					43				
14					44				
15					45				
16					46				
17					47				
18					48				
19					49				
20					50				
21					51				
22					52				
23					53				
24					54				
25					55				
26					56				
27					57				
28					58				
29					59				

I have received a copy of these opacity readings

_____

Evaluator's Signature:

_____

Title:_____ Date:_____

Figure 5-1. Visible Emission Observation form.

1204°C (2200°F). This temperature increases, however, to about 1427°C (2600°F) when the acid gas feed bypasses the Claus and tail gas unit and is routed directly to the incinerator, thus increasing SO_2 emissions at the stack. The incinerator temperature is a good indicator of the amount of acid gas being bypassed.

Completion of the Level I checklist is further discussed in Section 5.7.

5.3 LEVEL II INSPECTION

It is recommended that a Level II inspection be performed once every 6 to 9 months. The actual frequency depends on the workload and manpower available at the agency. The duration of the inspection depends on the size of the refinery and the number of inspectors. It takes a two-man team 1 to 2 days to inspect a 30,000 barrel per day integrated refinery. Before the inspection, obtain the data listed below for the units being inspected; during the inspection, review the data with refinery personnel.

- Process flow diagram
- Process information
- Heater and boiler data (type of fuel, heater duty, exit temperature, and stack data)
- Storage tank data
- Wastewater separator data (type of separator, type of cover, condition of cover)

Some fugitive emissions are monitored by a hydrocarbon detector, in addition to the monitoring of particulates and SO_2 emissions.

Review and investigate the following units:

Unit	Pollutant
Fluid catalytic cracking	Hydrocarbon vapors; particulates; sulfur dioxide
Sulfur recovery	Sulfur dioxide
Watewater treatment	Hydrocarbon vapors

(continued)

Unit	Pollutant
Isomerization	Hydrocarbon vapors, particulates
Alkylation	Hydrocarbon vapors, particulates
Storage	Hydrocarbon vapors
Loading	Hydrocarbon vapors
Light-ends/gas processing	Hydrocarbon vapors

The survey of oil refineries by the California Air Resources Board in April 1978 showed that isomerization, alkylation, storage, loading, light ends/gas processing, and FCC units accounted for about 40 percent of the fugitive hydrocarbon emissions. The CARB study also identified the items that contributed most to fugitive emissions: valves, pump seals, and compressor seals. For each process unit listed, use a hydrocarbon detector to inspect a certain number of the key emission contributors (Table 5-1). A screening procedure for monitoring fugitive emissions is provided in Appendix H. Appendix G contains operating instructions for a Century Organic Vapor Analyzer, hydrocarbon detector.

5.4 LEVEL III INSPECTION

It is recommended that a Level III inspection be performed once every 12 to 18 months. The frequency and duration depends on the workload and manpower available at the agency. The duration of the inspection depends on the size and complexity of the refinery. It takes a four-man team about one week to inspect a 30,000 barrel per day integrated refinery. It is a very detailed inspection of the following units:

TABLE 5-1. LEVEL II LEAK DETECTION PROGRAM

Process unit	Valves (in gas service)		Pump seals		Compressor seals	
	Sample size	Accept No.*	Sample size	Accept No.*	Sample size	Accept No.*
Isomerization	20	5				
Alkylation	20	5	5	1		
Storage	20	5	8	2	2	1
Loading	20	5	8	2		
Gas processing	20	5	8	2	2	1
FCC	8	2	5	1	2	1

*The accept number is the maximum number of leaks detected in the sample size that results in statistically approving the sample. This number is based on varying quality levels and statistics. Appendix E explains the derivation of these numbers.

Unit	Pollutant
Fluid catalytic cracking	Hydrocarbon vapors; particulates, sulfur dioxide
Sulfur recovery	Sulfur dioxide
Wastewater treatment	Hydrocarbon vapors
Distillation: Vacuum	Hydrocarbon vapors; particulates
Distillation: Atmospheric	Hydrocarbon vapors; particulates
Isomerization	Hydrocarbon vapors; particulates
Alkylation	Hydrocarbon vapors; particulates
Storage	Hydrocarbon vapors
Loading	Hydrocarbon vapors
Light-ends/gas processing	Hydrocarbon vapors
Hydrocracking	Hydrocarbon vapors; particulates
Reforming	Hydrocarbon vapors; particulates
Visbreaking	Hydrocarbon vapors
Hydrotreating (Hydrodesulfurization, or HDS)	Hydrocarbon vapors

Again, the CARB study determined that the process units listed above comprise about 52 percent of the fugitive hydrocarbon emissions. For each process unit listed, use a hydrocarbon sniffer to inspect a certain number of the key emission contributors (Table 5-2). The operating instructions for using a Century Organic Vapor Analyzer to monitor fugitive emissions is provided in Appendix G. Appendix H contains a screening procedure for monitoring fugitive emissions.

5.5 INSPECTION SCHEDULE

Table 5-3 shows a proposed schedule of inspections by level for an individual refinery; it can be used as a guideline for planning an inspection program. The inspector may decide to

TABLE 5-2 LEVEL III LEAK DETECTION PROGRAM

Process unit	Valves (in gas service)		Pump seals		Compressor seals	
	Sample size	Accept No.	Sample size	Accept No.	Sample size	Accept No.
Isomerization	20	2				
Alkylation	50	5	8	1		
Storage	50	5	20	2	3	0
Loading	50	5	20	2		
Gas Processing	50	5	20	2	3	0
FCC	20	2	8	1	3	0
Visbreaking	20	2	8	1	3	0
Hydrotreating* (HDS)	20	2	8	1	3	0
Hydrocracking	20	2	8	1	3	0
Reformer	20	2	8	1	3	0
Distillation: Atmospheric	20	2	8	1		
Distillation: Vacuum	20	2	8	1		

*A refinery has hydrotreating units for several feedstreams, some of which are listed below:

HDS--reformer feed
HDS--light gas oil
HDS--heavy gas oil
Vacuum--(Residue) gas oil
Coker--Naphtha

TABLE 5-3 EXAMPLE OF AN INSPECTION SCHEDULE FOR AN INDIVIDUAL REFINERY

Month	Inspection level
February	Level I
April	Level II
June	Level I
July	Level III
September	Level I
November	Level II

perform a higher level of inspection on the basis of recurring violations or specific problems. For example, an inspector may notice a problem with the FCC unit while conducting a Level I inspection. The inspector identifies the problem by obtaining additional Level III information, then proceeds with the Level I inspection of the other units.

5.6 INSPECTION REPORT FORM

Complete an Inspection Report form, as shown Figure 5-2, on a separate sheet. This form is used as a cover page for each inspection report. Attach to the sheet the completed unit checklists. The cover sheet, the completed checklists, and any pertinent notes, comments, or records constitute your complete inspection report. The local, state, or federal policies may dictate the information on these proposed checklists be transferred to a designated form.

5.7 COMPLETION OF LEVEL I CHECKLIST

A blank checklist of a Level I inspection is shown in Figure 5-3. A copy is also provided in Appendix J. Sample checklists have been completed to show the result before and after the inspection.

From a file search prior to the inspection, the inspector knows the number and type of cracking and sulfur units in the refinery. A hypothetical refinery has one fluid catalytic cracking unit with a refinery identification of 212, as shown in Figure 5-4. The types of control, as found during the inspection and shown in Figure 5-5, are one ESP, six internal cyclones in the reactor, six internal cyclones in the regenerator, and a CO boiler. The opacity of the FCC sump stack is also recorded in the checklist at this time. The control equipment that is not operating at the time of the inspection should be listed in the checklist.

I. Heater and Boiler Information

Identification Number	Heater description including unit location	Opacity	Comments
H-1	Crude unit		
H-2	Crude unit		
H-3	FCC		
H-4	Reformer		
H-5	Reformer		
B-1	Steam Generation		
B-2	Steam Generation		

II. Catalytic Cracker

Identification Number or Name	Type of Process	Pollution Control Equipment			FCC Sump Stack Opacity	Comments
		CO Boiler	ESP	Cyclones		
FCC 212	Fluid					

III. Sulfur Plant

Identification Number or Name	Pollution Control Equipment	Incinerator Temperature (°F)	Incinerator Stack Opacity	Comments
SP 300				

IV. General Comments

(Note the general housekeeping practices of the refinery.)

Figure 5-4. Example Level I inspection checklist after file research.

I. Heater and Boiler Information

Identification Number	Heater description including unit location	Opacity (%)	Comments
H-1	Crude unit	0	
H-2	Crude unit	-	Not operating
H-3	FCC	10	
H-4	Reformer	0	
H-5	Reformer	0	
B-1	Steam Generation	0	
B-2	Steam Generation	0	

II. Catalytic Cracker

Identification Number or Name	Type of Process	Pollution Control Equipment (CO Boiler) (ESP) Cyclones	FCC Sump Stack Opacity (%)	Comments
FCC 212	Fluid	6 cyclones regenerator 6 cyclones reactor	0	

III. Sulfur Plant

Identification Number or Name	Pollution Control Equipment	Incinerator Temperature (°F)	Incinerator Stack Opacity (%)	Comments
SP 300	Claus unit	2200°F	10	

IV. General Comments

Roads were not paved.

Figure 5-5. Example Level I inspection checklist after inspection.

The Level I data needed for the checklist for a sulfur plant includes the unit number or name, the control equipment, the incinerator temperature (°F), and the incinerator stack opacity. At the time of the inspection, the inspector should ask plant personnel about the type of control equipment, temperature, and stack opacity.

Heater and boiler description and unit location can usually be obtained in the state files prior to an inspection. At the time of the inspection, the inspector should verify the heater and boiler information and record the opacity of the stacks. In the hypothetical refinery, one of the heaters was not operating during the inspection. This should be noted on the checklist (as shown in Figure 5-5).

5.8 COMPLETION OF LEVEL II CHECKLIST

A Level II checklist includes a more detailed description of each process unit, storage tank data, and wastewater treatment facilities, in addition to heater and boiler information. Blank and completed checklists are presented in Appendixes K and L.

Prior to the inspection, an inspector may be able to search files for descriptions of process units, storage tanks, and loading facilities. During the inspection, the inspectors should observe each of the process units to verify the process descriptions obtained in the file search. All heaters and boilers should also be observed to record opacity. The data on storage tanks should be verified. Appendix D contains the vapor pressure of common petrochemical compounds found in petroleum refineries. This information is useful in completing the "Storage Tank Data" sheet of the checklist. While inspecting the wastewater treatment facility, the inspector should note on the checklist any odors and whether the separator is adequately covered.

The second part of the inspection includes the screening of selected units with a hydrocarbon detector. The data are recorded on a leak detection survey log (appearing as blank forms in

Appendix K and as a completed form in Appendix L). All the information on the form must be completed while at the refinery.

5.9 COMPLETION OF LEVEL III CHECKLIST

The completion of the Level III checklist provides a very detailed description of the refinery. This checklist includes all the information from the Level II checklist plus a screening survey of 10 units in the refinery and additional process data.

The checklist and leak detection survey log are completed in the same manner as the Level II checklist shown in Appendix L. A blank checklist for a Level III checklist is presented in Appendix M.

LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 20

Unit Isomerization

Accept No. 5

Component Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Unit Alkylation

Component Valves

Sample size 20

Accept No. 5

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 5

Unit Alkylation

Accept No. 1

Component Pump seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Unit Storage

Component Valves

Sample size 20

Accept No. 5

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 8

Unit Storage

Accept No. 2

Component Pump seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: II

Sample size: 2

Unit: Storage

Accept No.: 1

Component: Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 20

Unit Loading

Accept No. 5

Component Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Unit Loading

Component Pump seals

Sample size 8

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Unit Gas processing

Component Valves

Sample size 20

Accept No. 5

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Unit Gas processing

Component Pump seals

Sample size 8

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: II

Sample size: 2

Unit: Gas processing

Accept No.: 1

Component: Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: II

Unit: FCC

Component: Valves

Sample size: 8

Accept No.: 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level II

Unit FCC

Component Pump seals

Sample size 5

Accept No. 1

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: II

Sample size: 2

Unit: FCC

Accept No.: 1

Component: Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

APPENDIX L

LEVEL II INSPECTION: EXAMPLE COMPLETED CHECKLIST FORMS

This appendix provides an example of a completed Level II checklist.

LEVEL II INSPECTION

AQCR 003

Date(s) of Inspection March 17-18, 1980

Time In 8:00/9:00 Out 4:00/2:00

Company Name Refinery A

Mailing Address 201 Oil Blvd. Oil City, U.S.A.

Location of Facility County

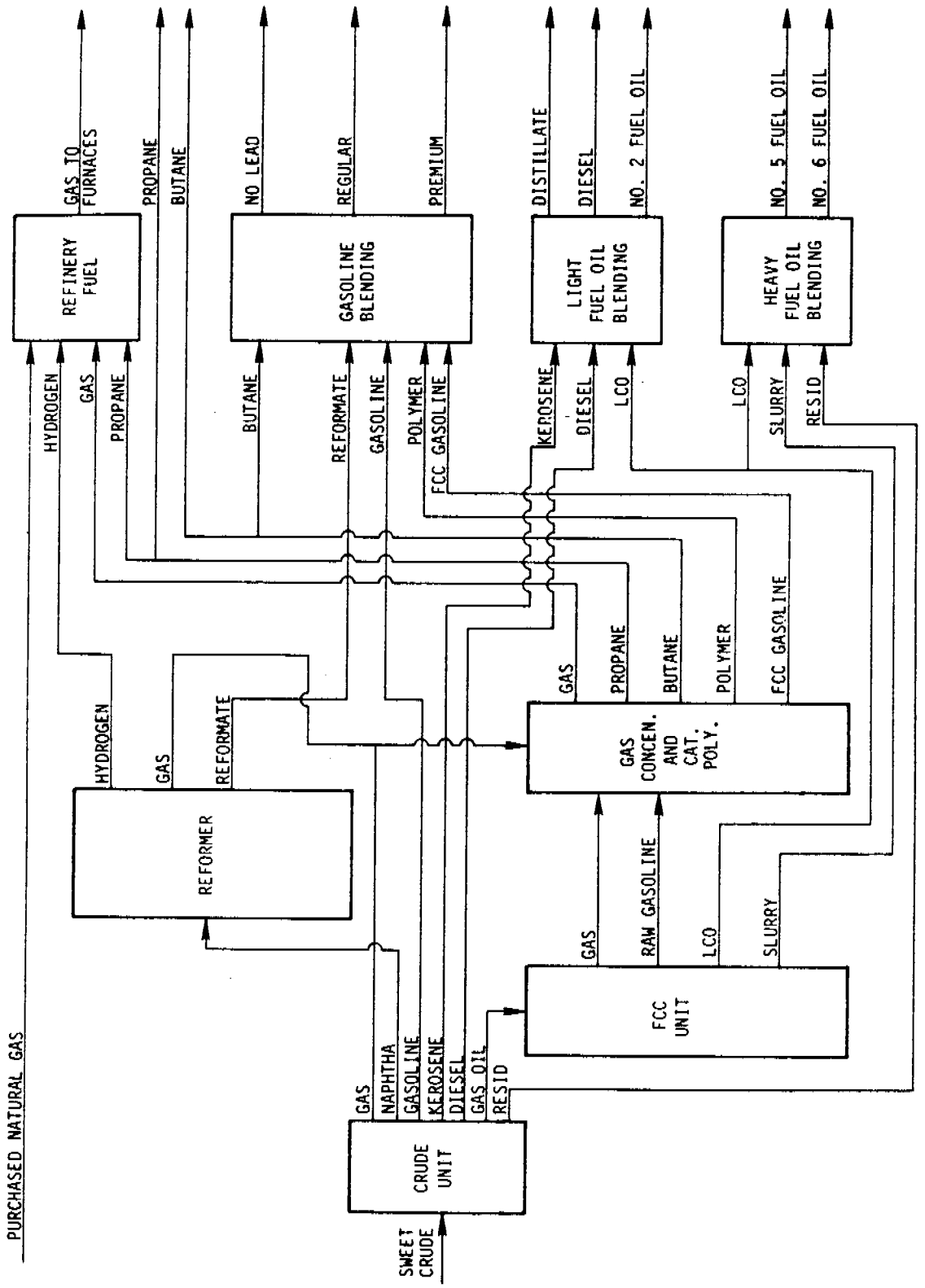
(Include County or Parish)

Type of Industry Petroleum Refinery

Form of Ownership

Corporate Address

Company Personnel	Name	Title	Phone
Responsible for Facility		Refinery Manager	
Responsible for Environmental Matters		Assistant Manager	
Company Personnel Contacted		Refinery Manager	
Confidentiality Statement given to			
EPA Personnel			
State or Local Agency Personnel			



REFINERY FLOW DIAGRAM

FCC: FLUID CATALYTIC CRACKING
LCO: LIGHT CYCLE OIL

PROCESS INFORMATION

Process unit	Number of units	Identification number or name	Process description	Refinery terminology
Crude distillation	1	212	Number of atmospheric towers - 2 Description of towers - preflash, primary, secondary, tertiary fractionating towers Number of atmospheric towers - Description of towers - preflash, primary, secondary, tertiary fractionating towers	
Vacuum distillation	1		Pressure of tower - 10 mm Hg absoulte Type of vacuum producing system - 3 stage job 1 contact condenser 1 surface condenser Pressure of tower Type of vacuum producing system	
Catalytic reforming	1	300	3 Fixed bed reactors	Powerformer
Isomerization			Type - Catalyst -	

PROCESS INFORMATION

Process unit	Feed	Products	Maximum rate, barrels/day	Current rate, barrels/day	Evaluated for RACT particulates, carbon monoxide sulfur oxide	Pollution abatement equipment
Crude distillation	Sweet crude	Gas Naphtha Kerosene Diesel Gas oil		20,000		
Vacuum distillation	Atmospheric bottoms	Gas oil Resid		5,000		
Catalytic reforming	Naphtha	Hydrogen Gas Reformate		3,100		
Isomerization						

PROCESS INFORMATION

Process unit	RACT requirements	Comments
Crude distillation		
Vacuum distillation	All hot wells must be covered 1 covered hot well	Hydrocarbon vapors from surface condensers are flared.
Catalytic reforming	Recommended venting to atmosphere after 5 psig during turnaround Last shutdown date February, 1980 Next shutdown date	
Isomerization	Last shutdown date Next shutdown date	

PROCESS INFORMATION

Process unit	Number of units	Identification number or name	Process description	Refinery terminology
Polymerization	1	400	Type - Solid phosphonic acid Catalyst -	
Alkylation			Type of process -	
Hydrocracking				
Catalytic cracking	1	500	Type of process - Fluid - UOP design	
Coking			Type of process -	
Visbreaking				
Deasphalting			Solvent employed	

PROCESS INFORMATION

Process unit	Feed	Products	Maximum rate, barrels/day	Current rate, barrels/day	Evaluated for RACT particulates, carbon monoxide sulfur oxide	Pollution abatement equipment
Polymerization	Gas Raw gasoline	Gas Propane Butane Polymer		2,000		
Alkylation						
Hydrocracking						
Catalytic cracking	Gas oil and wax crude oil	Gas Raw gasoline Slurry		7,000		Primary and secondary cyclones 99.9 percent efficiency
Coking						
Visbreaking						
Deasphalting						

PROCESS INFORMATION

Process unit	RACT requirements	Comments
Polymerization	Last shutdown date February, 1980 Next shutdown date	
Alkylation		
Hydrocracking		
Catalytic cracking		Installed 1958
Coking		
Visbreaking		
Deasphalting		

PROCESS INFORMATION

Process unit	Number of units	Identification number or name	Process description	Refinery terminology
Hydrotreating	1	600		
Wax production				
Grease production				
Lube production				
Asphalt				
Gas processing				
Sulfur plant	1	700	Amine treating and claus sulfur plant	
Furfural extraction				

PROCESS INFORMATION

Process unit	Feed	Products	Maximum rate, barrels/day	Current rate, barrels/day	Evaluated for RACT particulates, carbon monoxide sulfur oxide	Pollution abatement equipment
Hydrotreating						
Wax production						
Grease production						
Lube production						
Asphalt						
Gas processing						
Sulfur plant	Sour waste gas	Sulfur		10 tons/day		
Furfural extraction						

PROCESS INFORMATION

Process unit	RACT requirements	Comments
Hydrotreating		
Wax production		
Grease production		
Lube production		
Asphalt		
Gas processing		
Sulfur plant		
Furfural extraction		

PROCESS INFORMATION

Process unit	Number of units	Identification number or name	Process description	Refinery terminology
Amine treating	1	Sulfur plant	Type of solvent - Monoethgnolamine (MEA)	
Other				

PROCESS INFORMATION

Process unit	Feed	Products	Maximum rate, barrels/day	Current rate, barrels/day	Evaluated for RACT particulates, carbon monoxide sulfur oxide	Pollution abatement equipment
Amine treating						
Other						

PROCESS INFORMATION

Process unit	RACT requirements	Comments
Amine treating		
Other		

HEATER AND BOILER INFORMATION

Identification No.	Heater description, including unit location	Fuel capability	Current fuel	Duty, million Btu/h		Number of stacks	Stack data		
				Maximum	Current		Height, ft	Diameter, ft	Exit temp., °F
H-1	Crude distillation unit		1, 2	40		2	55	3.0	350
H-2	Crude distillation unit		1, 2	20		2	95	6.0	350
H-3	Reformer		3	15		1	40	4.0	800
H-4	Reformer		3	15		2	40	3.5	800
H-5	FCC		3	8		2	50	3.0	1200

1 = Refinery gas. 2 = Natural gas. 3 = No. 6 Fuel oil.

HEATER AND BOILER INFORMATION (continued)

Identification No.	Heater description including unit location	Opacity
H-1	Crude distillation unit	0
H-2	Crude distillation unit	0
H-3	Reformer	0
H-4	Reformer	10
H-5	FCC	0

For Particulate, sulfur dioxide, and nitrogen oxide emission information.

Type of Fuel used in Boilers and Heaters	Heat Content Btu/lb or Btu/scf	Sulfur Content
Refinery gas	800 Btu/scf	100 grains H_2S/scf
No. 6 Fuel oil	6 Btu/bbl	0.9%

TANK INFORMATION

Tank Number	Capacity (Units)	Type (1)	Product Stored	True Vapor Pressure (Units) psia	Tank Color	Construction: Welded or Riveted	Vapor Controls (2)	Remarks*
1	600	C	Crude oil	2.2	Gray	Welded	F	
2	600	C	Crude oil	2.2	Gray	Welded	F	
3	100	C	Gas oil	<1.0	Gray	Welded	N	
4	100	C	Gas oil	<1.0	Gray	Welded	N	
5	100	C	Gas oil	<1.0	Gray	Welded	N	
6	25	C	Diesel	0.2	Gray	Welded	N	
7	75	C	Unleaded gasoline	5-12	Gray	Welded	VR	Vapor recovery compressor system
8	75	C	Unleaded gasoline	5-12	Gray	Welded	VR	Vapor recovery compressor system
9	560	C	Regular gasoline	5-12	Gray	Welded	VR	Vapor recovery compressor system
10	560	C	Regular gasoline	5-12	Gray	Welded	VR	Vapor recovery compressor system

Footnotes:

(1) C = fixed roof: F = floating roof; P = pressure; O = open top; S = spheroid; H = horizontal; U = underground

(2) N = None, CV = conservation vents; F = floating roof (SS = single seal; DS = double seal); VR = Vapor recovery (describe); VD = vapor disposal (describe); VB = vapor balance; SF = submerged fill

* Date installed, etc.

VOLATILE HYDROCARBON LOADING/UNLOADING FACILITIES

LOADING FACILITY DESIGNATION	SOURCE	TYPE TRANSFER/SIZE (RR CARS, TRUCKS)	MONTHLY THRU-PUT (1000 GAL)	VAPOR CONTROL SYSTEM	SUBMERGED LOADING	PRODUCTS	
						TYPE	VAPOR PRESSURE (PSIA)
Loading		Truck	1,500		yes (100%)	Gasoline	10
Loading		Truck	1,560		no	Propane Butane	200 60

WASTEWATER TREATMENT

Treatment facility	Observations				
In-plant treatment: Sour water stripper	Noticeable emissions[a] Yes No	Disposition of sulfides[a] Incinerated Recovered in sulfur recovery unit			
Primary treatment: Gravity separators	Type(s) of separator 3 API	Gaps (or) leaks in cover: Inspect with hydrocarbon detector 2 1	a Covered Uncovered	Type of cover fabric	Noticeable emissions[a] Yes (No)
Intermediate treatment: Dissolved air flotation unit and holding basin	Type(s)	Capacity of each			
Secondary treatment: Biological oxidation	Type(s)	Capacity of each			
Tertiary treatment	Type(s)	Capacity of each			
Solids disposal	Type(s)	Disposal[a] Onsite Offsite			
Surge storage capability	Type(s)	Capacity of each			

[a] Circle one.

LEAK DETECTION SURVEY LOG

Inspection level: II

Unit: Gas Processing

Component: Valves

Sample size: 20

Accept No.: 5

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	
Gate valve	X		X		100 ppm
Gate valve	X		X		40 ppm
Control globe valve	X		X		100 ppm

APPENDIX M

LEVEL III INSPECTION: BLANK CHECKLIST FORMS

This appendix provides the cover sheet and additional forms to be used in conducting a Level III inspection. When combined with the Level II checklist forms (Appendix K), this material constitutes a Level III inspection report.

LEVEL __ INSPECTION

AQCR _____ Date(s) of Inspection _____

_____

Time In _____ Out _____

Company Name _____

Mailing Address _____

_____

Location of Facility _____

_____

(Include County or Parish)

Type of Industry _____

Form of Ownership _____

Corporate Address _____

_____

Company Personnel	Name	Title	Phone
Responsible for Facility			
Responsible for Environmental Matters			
Company Personnel Contacted			
Confidentiality Statement given to			
EPA Personnel			
State or Local Agency Personnel			

ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTIONS

Process unit		
Crude distillation		
Vacuum distillation	Number of ejectors	
	Type of ejectors	
	Type of condensers	
	Is hot well covered?	
Catalytic cracking	Reactor temperature, °F	
	CO boiler temperature, °F	
	Oxygen analyzer, % O_2	
	ESP status:	
	Primary voltage, kW	
	Primary current, amp	
	Secondary current, amp	
	Hopper heaters (on, off)	
	Hopper level indicators (full, empty)	
Isomerization	Reactor temperature, °F	

ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTIONS

Process unit		
Polymerization	Reactor temperature, °F	
Alkylation	Reactor temperature, °F	
Hydrocracking		
Catalytic reforming	Reactor temperature, °F Reactor pressure, psig Hydrogen pressure, psig	
Coking		

ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTION

Process unit		
Visbreaking		
Deasphalting		
Hydrotreating	Reactor temperature, °F Reactor pressure, psig Hydrogen pressure, psig	
Wax production		
Grease production		

ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTION

Process unit		
Lube production		
Asphalt		
Gas processing		
Sulfur plant	Air/acid gas ratio Air/stripper gas ratio Inlet catalytic reactor temperature, °F Outlet catalytic reactor temperature, °F Incinerator temperature, °F	
Furfural refining		

ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTION

Process unit		
Amine treating	Hydrocarbon in acid gas feed	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Isomerization

Component Valves

Sample size 20

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: III

Sample size: 50

Unit: Alkylation

Accept No.: 5

Component: Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Alkylation

Component Pump seals

Sample size 8

Accept No. 1

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 50

Unit Storage

Accept No. 5

Component Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Storage

Component Pump seals

Sample size 20

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Storage

Accept No. 0

Component Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Loading

Component Valves

Sample size 50

Accept No. 5

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Loading

Component Pump seals

Sample size 20

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: III

Sample size: 50

Unit: Gas processing

Accept No.: 5

Component: Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 20

Unit Gas processing

Accept No. 2

Component Pump seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Gas processing

Accept No. 0

Component Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit FCC

Component Valves

Sample size 20

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: III

Unit: FCC

Component: Pump seals

Sample size: 8

Accept No.: 1

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit FCC

Component Compressor seals

Sample size 3

Accept No. 0

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: III

Sample size: 20

Unit: Visbreaking

Accept No.: 2

Component: Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Visbreaking

Component Pump seals

Sample size 8

Accept No. 1

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Visbreaking

Accept No. 0

Component Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 20

Unit Hydrotreating

Accept No. 2

Component Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level: III

Sample size: 8

Unit: Hydrotreating

Accept No.: 1

Component: Pump seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrotreating

Component Compressor seals

Sample size 3

Accept No. 0

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrocracking

Component Valves

Sample size 20

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrocracking

Component Pump seals

Sample size 8

Accept No. 1

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Hydrocracking

Accept No. 0

Component Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Reformer

Component Valves

Sample size 20

Accept No. 2

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Unit Reformer

Component Pump seals

Sample size 8

Accept No. 1

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Reformer

Accept No. 0

Component Compressor seals

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 20

Unit Distillation - atmospheric

Accept No. 2

Component Valves

Description of source	Stream composition		Stream volatility		Maximum VOC reading
	Gas	Liquid	High	Low	

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REVISED EPA TRACEABILITY PROTOCOLS 1 AND 2

The Quality Assurance Division, Environmental Monitoring Systems Laboratory of the U. S. EPA at the Research Triangle Park, North Carolina, has revised Traceability Protocols 1 and 2 for preparation of gas standards. Organizations selling Protocols 1 or 2 standards or preparing them for their own use must now follow the revised protocols. A copy of each revised protocol is attached. Revised Protocol 1 allows only one procedure (G-1) for the assay and certification of compressed gas standards used on continuous source emission monitors. Revised Protocol 2 allows two procedures (G-1 and G-2) for the assay and certification of compressed gas standards and two procedures (P-1 and P-2) for the assay and certification of permeation device standards used on ambient air pollution analyzers.

The significant changes in the revised Protocols 1 and 2 compared to the original Protocols 1 and 2 they replace are as follows:

1. The recertification limit for compressed gas standards for SO_2, NO, CO, CO_2 and O_2 in aluminum or stainless steel cylinders has been increased to 18 months. In the original protocols the limits were 6 months for SO_2, NO, and CO, and 12 months for CO_2 and O_2.

2. Two procedures have been described for the assay and certification of compressed gas standards. Procedure G-1 is without dilution and Procedure G-2 is with dilution. Only Procedure G-1 is allowed for Protocol 1. Procedures G-1 and G-2 are allowed for Protocol 2. However, Procedure G-1 is always preferred over Procedure G-2 since less error will result. Only a procedure similar to G-1 were in the original Protocols 1 and 2.

3. Two procedures have been described for the assay and certification of permeation devices. Procedure P-1 references the candidate device to an NBS SRM permeation device. Procedure P-2 references the candidate device to a compressed gas standard. Only a procedure similar to P-1 was in the original Protocol 2.

As stated in Protocol 1 (Section 4.0.9) and Protocol 2 (Section 7.0.11), it is the intention of the U. S. EPA to periodically assess the accuracy of commercially available compressed gas and permeation device standards that have been assayed and certified according to these protocols. The accuracy of the procured standards and the names of the commercial manufacturers will be published as public information.

Please distribute these revised protocols to those individuals who need them. In the near future, revised Protocol 1 will be published and distributed as Section 3.0.4 of Volume III (Stationary Source Specific Methods) of the Quality Assurance Handbook for Air Pollution Measurement Systems (EPA-600/4-77-027b). Revised Protocol 2 will be published and distributed as Section 2.0.7 of Volume II (Ambient Air Specific Methods) of the Quality Assurance Handbook for Air Pollution Measurement Systems (EPA-600/4-77-027a).

July 10, 1987

3.0.4. PROCEDURE FOR NBS-TRACEABLE CERTIFICATION OF COMPRESSED GAS WORKING STANDARDS USED FOR CALIBRATION AND AUDIT OF CONTINUOUS SOURCE EMISSION MONITORS (Revised Traceability Protocol No. 1)

CONTENTS

Subsection	Title	Pages
3.0.4.0	General Information	1 to 8
3.0.4.1	Procedure G1: Assay and Certification of a Compressed Gas Standard Without Dilution	G1-1 to G1-5
3.0.4.2	References	

4.0 GENERAL INFORMATION

4.0.1 Purpose and Scope of the Procedure

Section 3.0.4 describes a procedure for assaying the concentration of gaseous pollutant concentration standards and certifying that the assay concentrations are traceable to an authoritative reference concentration standard. This procedure is recommended for certifying the local working concentration standards required by the pollutant monitoring regulations of 40 CFR Part 60[1,2] for the calibration and audit of continuous source emission monitors. The procedure covers certification of compressed gas (cylinder) standards for CO, CO_2, NO, NO_2, and SO_2 (Procedure G1).

4.0.2 Reference Standards

Part 60 of the monitoring regulations[1,2] require that working standards used for calibration and audit of continuous source emission monitors be traceable to either a National Bureau of Standards (NBS) gaseous Standard Reference Material (SRM) or a NBS/EPA-approved Certified Reference Material (CRM)[3]. Accordingly, the reference standard used for assaying and certifying a working standard for these purposes must be an SRM, a CRM, or a suitable intermediate standard (see the next paragraph). SRM cylinder gas standards available from NBS are listed in Table 7.2 at the end of subsection 4.0. A current list of CRM cylinder gases and CRM vendors is available from the Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U. S. EPA, Research Triangle Park, NC 27711.

The EPA regulations define a "traceable" standard as one which "...has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as a...NBS [gaseous] SRM or...CRM"[4,5]. Certification of a working standard directly to an SRM or CRM primary standard is, of course, preferred and recommended because of the lower error. However, an intermediate reference standard is permitted, if necessary. In particular, a Gas Manufacturer's Intermediate Standard (see subsection 4.0.2.1) that has been referenced directly to an SRM or a CRM according to Procedure G1 is an acceptable intermediate standard and could be used as the reference standard on that basis. However, purchasers of com-

mercial gas standards referenced to an intermediate standard such as a GMIS should be aware that, according to the above definition, such a standard would have to be used directly for calibration or audit. Since a second intermediate standard is not permitted, such a standard could not be used as a reference standard to certify other standards.

4.0.2.1 Gas Manufacturer's Intermediate Standard (GMIS). A GMIS is a compressed (cylinder) gas standard that has been assayed with direct reference to an SRM or CRM and certified according to Procedure G1, and also meets the following requirements:

1. A candidate GMIS must be assayed a minimum of three (3) times, uniformly spaced over a three (3) month period.

2. Each of the three (or more) assays must be within 1.0 percent of the mean of the three (or more) assays.

3. The difference between the last assay and the first assay must not exceed 1.5 percent of the mean of the three (or more) assays.

4. The GMIS must be recertified every three months, and the reassay must be within 1.5 percent of the previous certified assay. The recertified concentration of the GMIS is the mean of the previous certified concentration and the reassay concentration.

4.0.2.2 Recertification of Reference Standards. Recertification requirements for SRMs and CRMs are specified by NBS and NBS/EPA, respectively. See 4.0.2.1 for GMIS recertification requirements.

4.0.3 Using the Procedure

The assay/certification procedure described here is carefully designed to minimize both systematic and random errors in the assay process. Therefore, the procedure should be carried out as closely as possible to the way it is described. Similarly, the assay apparatus has been specifically designed to minimize errors and should be configured as closely as possible to the design specified. Good laboratory practice should be observed in the selection of inert materials (e.g. Teflon, stainless steel, or glass, if possible) and clean, non-contaminating components for use in portions of the apparatus in contact with the candidate or reference gas concentrations.

4.0.4 Certification Documentation

Each assay/certification must be documented in a written certification report signed by the analyst and containing at least the following information:

1. Identification number (cylinder number).

2. Certified concentration of the standard, in ppm or mole percent.

3. Balance gas in the standard mixture.

4. Cylinder pressure at certification.

5. Date of the assay/certification.

6. Certification expiration date (see 4.0.6.3).

7. Identification of the reference standard used: SRM number, cylinder number, and concentration for an SRM; cylinder number and concentration for a CRM or GMIS.

8. Statement that the assay/certification was performed according to this Section 3.0.4.

9. Identification of the laboratory where the standard was certified and the analyst who performed the certification.

10. Identification of the gas analyzer used for the certification, including the make, model, serial number, the measurement principle, and the date of the last multipoint calibration.

11. All analyzer readings used during the assay/certification and the calculations used to obtain the reported certified value.

12. Chronological record of all certifications for the standard.

Certification concentrations should be reported to 3 significant digits. Certification documentation should be maintained for at least 3 years.

4.0.5 Certification Label

A label or tag bearing the information described in items 1 through 9 of subsection 4.0.4 must be attached to each certified gas cylinder.

4.0.6 Assay/Certification of Compressed Gas (Cylinder) Standards

4.0.6.1 Aging of newly-prepared gas standards. Freshly prepared gas standard concentrations and newly filled gas cylinders must be aged before being assayed and certified. SO_2 concentrations contained in steel cylinders must be aged at least 15 days; other standards must be aged at least 4 days.

4.0.6.2 Stability test for reactive gas standards. Reactive gas standards, including nitric oxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and carbon monoxide (CO), that have not been previously certified must be tested for stability as follows: Reassay the concentration at least 7 days after the first assay and compare the two assays. If the second assay differs from the first assay by 1.5% or less, the cylinder may be considered stable, and the mean of the two assays should be reported as the certified concentration. Otherwise, age the cylinder for a week or more and repeat the test, using the second and third assays as if they were the first and second assays. Cylinders that are not stable may not be sold and/or used for calibration or audit purposes.

4.0.6.3 Recertification of compressed gas standards. Compressed gas standards must be recertified according to this Section 3.0.4 within the time limits specified in Table 7.1[3,6,7]. The reassay concentration must be within 5% of the previous certified concentration. If not, the cylinder must be retested for stability (subsection 4.0.6.2). The certified concentration of a recertified standard should be reported as the mean of all assays, unless a clear trend or substantial change suggests that previous assays are no longer valid.

Table 7.1 Recertification limits for compressed gas standards.

Pollutant	Balance gas	Concentration range	Maximum months until recertification for cylinder material: Al or SS	other
Carbon monoxide	N_2 or air	≥ 5 ppm	18	6
Nitric oxide	N_2	≥ 10 ppm	18	6
Sulfur dioxide	N_2	≥ 10 ppm	18	6
Nitrogen dioxide	N_2 or air	≥ 10 ppm	6	6
Carbon dioxide	N_2 or air	≥ 300 ppm	18	18
Oxygen	N_2	≥ 2 percent	18	18
Sulfur dioxide and carbon dioxide	N_2	≥ 200 ppm SO_2, ≥ 10 percent CO_2	18	6
Propane	N_2 or air	≥ 5 ppm	18	6
Others not specifically listed			6	6

4.0.6.4 Minimum cylinder pressure. No compressed gas cylinder standard should be used when its gas pressure is below 700 kPa (100 psi), as indicated by the cylinder pressure gauge.

4.0.6.5 Assay/certification of multi-component compressed gas standards. Procedure G1 may be used to assay and certify individual components of multi-component gas standards, provided that none of the components other than the component being assayed cause a detectable response on the analyzer.

4.0.7 Analyzer Calibration

4.0.7.1 Basic analyzer calibration requirements. The assay procedure described in this Section 3.0.4 employs a direct ratio referencing technique that inherently corrects for minor analyzer calibration variations (drift) and DOES NOT depend on the absolute accuracy of the analyzer calibration. What is required of the analyzer is as follows: 1) it must have a linear response to the pollutant of interest (see subsection 4.0.7.5), 2) it must have good resolution and low noise, 3) its response calibration must be reasonably stable during the assay/certification process, and 4) all assay concentration measurements must fall within the calibrated response range of the analyzer.

4.0.7.2 Analyzer multipoint calibration. The gas analyzer used for the assay/certification must have had a multipoint calibration within 3 months of its use when used with this procedure. This calibration is not used to quantitatively interpret analyzer readings during the assay/certification of the candidate gas because a more accurate, direct ratio comparison of the candidate concentration to the reference standard concentration is used. However, this multipoint calibration is necessary to establish the calibrated range of the analyzer and its response linearity.

The multipoint calibration should consist of analyzer responses to at least 5 concentrations, including zero, approximately evenly spaced over the concentration range. Analyzer response units may be volts, millivolts, percent of scale, or other measurable analyzer response units. The upper range limit of the calibrated range is determined by the highest calibration point used. If the analyzer has a choice of concentration ranges, the optimum range for the procedure should be selected and calibrated. Plot the calibration points and compute the linear regression slope and intercept. See subsection 4.0.7.5 for linearity requirements and the use of a mathematical transformation, if needed. The intercept should be less than 1 percent of the upper concentration range limit, and the correlation coefficient (r) should be at least 0.999.

4.0.7.3 Zero and span check and adjustment. On each day that the analyzer will be used for assay/certification, its response calibration must be checked with a zero and at least one span concentration near the upper concentration range limit. If necessary, the zero and span controls of the analyzer should be adjusted so that the analyzer's response (i.e. calibration slope) is within about ±5 percent of the response indicated by the most recent multipoint calibration. If a zero or span adjustment is made, allow the analyzer to stabilize for at least an hour or more before beginning the assay procedure, since some analyzers drift for a period of time following zero or span adjustment. If the analyzer is not in continuous operation, turn it on and allow it to stabilize for at least 12 hours before the zero and span check.

4.0.7.4 Pollutant standard for multipoint calibration and zero and span adjustment. The pollutant standard or standards used for multipoint calibration or zero and span checks or adjustments must be obtained from a compressed gas standard certified traceable to an NBS SRM or a NBS/EPA CRM according to Procedure G1 of this Section 3.0.4. This standard need not be the same as the reference standard used in the assay/certification. The zero gas must meet the requirements in subsection 4.0.8.

4.0.7.5 Linearity of analyzer response. The direct ratio assay technique used in Procedure G1 requires that the analyzer have a linear response to concentration. Linearity is determined by comparing the quantitative difference between a smoothly-drawn calibration curve based on all calibration points and a straight line drawn between zero and an upper reference point (see Figure 1). This difference is measured in concentration units, parallel to the concentration axis, from a point on the calibration curve to the corresponding point for the same response on the straight line.

For the general linearity requirement, the straight line is drawn between zero and the highest calibration point (Figure 1a). Linearity is then acceptable when no point on the smooth calibration curve deviates from the straight line by more than 1.5 percent of the value of the highest calibration concentration. An alternative linearity requirement is defined on the basis of the actual reference and candidate concentrations to be used for the assay. In this case, the reference and candidate concentrations are plotted on the calibration curve, and the straight line is drawn from zero to the reference concentration and extrapolated, if necessary, beyond the candidate concentration (Figure 1b). The deviation of the smooth calibration curve from the straight line at the candidate concentration point then must not exceed 0.8 percent of the value of the reference concentration. This latter specification may allow the use of an analyzer having greater nonlinearity when the reference and candidate concentrations are nearly the same.

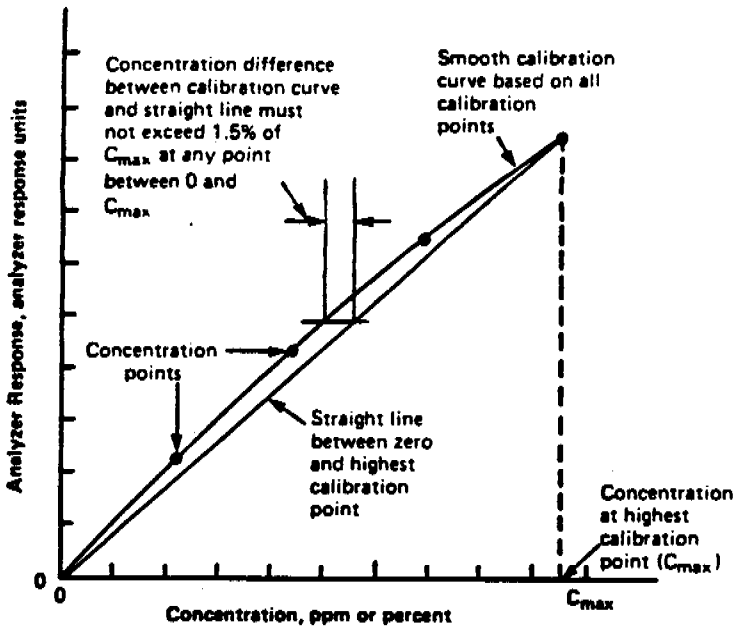
For analyzers having an inherently non-linear response, the response can usually be linearized with a simple mathematical transformation of the response values, such as R'= square root(R) or R'= log(R), where R' is the transformed response value and R is the actual analyzer response value. Using the transformed response values, the multipoint calibration should meet one of the above linearity requirements as well as the requirements for intercept and correlation coefficient given in subsection 4.0.7.2.

4.0.8 Zero Gas

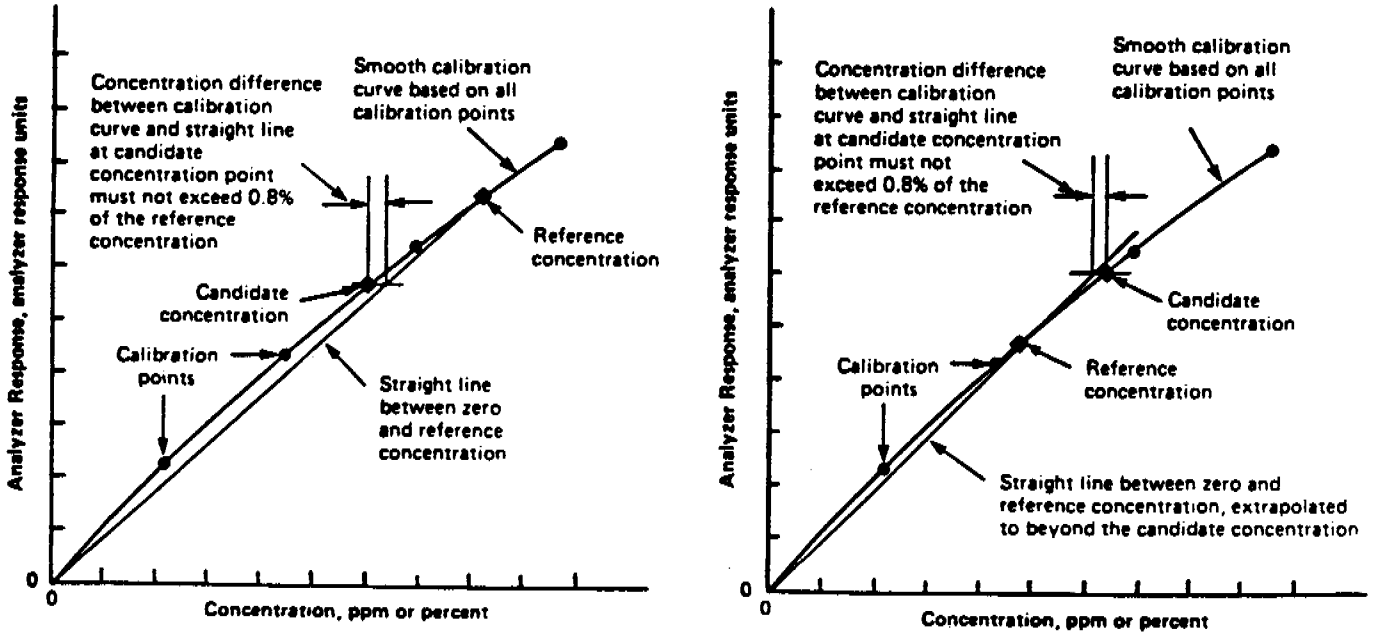
Zero gas used for dilution of any candidate or reference standard should be clean, dry, zero-grade air or nitrogen containing a concentration of the pollutant of interest equivalent to less than 0.5 percent of the analyzer's upper range limit concentration. The zero gas also should contain no contaminant that causes a detectable response on the analyzer or that suppresses or enhances the analyzer's response to the pollutant. The oxygen content of zero air should be the same as that of ambient air.

4.0.9 Accuracy Assessment of Commercially Available Standards

Periodically, the USEPA will assess the accuracy of commercially available compressed gas standards that have been assayed and certified according to this Section 3.0.4. Accuracy will be assessed by EPA audit analysis of representative actual commercial standards obtained via an anonymous agent. The accuracy audit results, identifying the actual gas manufacturers or vendors, will be published as public information.



a) General linearity requirement



b) Alternative linearity requirement

Figure 1. Illustration of linearity requirements.

Table 7.2. NBS SRM reference gases.

SRM number	Type	Nominal concentration		SRM number	Type	Nominal concentration	
2627	NO/N_2	5	ppm	1693	SO_2/N_2	50	ppm
2628	NO/N_2	10	ppm	1694	SO_2/N_2	100	ppm
2629	NO/N_2	20	ppm	1661a	SO_2/N_2	500	ppm
1683b	NO/N_2	50	ppm	1662a	SO_2/N_2	1000	ppm
1684b	NO/N_2	100	ppm	1663a	SO_2/N_2	1500	ppm
1685b	NO/N_2	250	ppm	1664a	SO_2/N_2	2500	ppm
1686b	NO/N_2	500	ppm	1696	SO_2/N_2	3500	ppm
1687b	NO/N_2	1000	ppm				
2630	NO/N_2	1500	ppm	1670	CO_2/Air	330	ppm
2631	NO/N_2	3000	ppm	1671	CO_2/Air	340	ppm
				1672	CO_2/Air	350	ppm
2653	NO_2/Air	250	ppm				
2654	NO_2/Air	500	ppm	2632	CO_2/N_2	300	ppm
2655	NO_2/Air	1000	ppm	2633	CO_2/N_2	400	ppm
2656	NO_2/Air	2500	ppm	2634	CO_2/N_2	800	ppm
				2619a	CO_2/N_2	0.5	percent
2612a	CO/Air	10	ppm	2620a	CO_2/N_2	1.0	percent
2613a	CO/Air	20	ppm	2621a	CO_2/N_2	1.5	percent
2614a	CO/Air	45	ppm	2622a	CO_2/N_2	2.0	percent
				2623a	CO_2/N_2	2.5	percent
1677c	CO/N_2	10	ppm	2624a	CO_2/N_2	3.0	percent
2635	CO/N_2	25	ppm	2625a	CO_2/N_2	3.5	percent
1678c	CO/N_2	50	ppm	2626a	CO_2/N_2	4.0	percent
1679c	CO/N_2	100	ppm	1674b	CO_2/N_2	7.0	percent
2636	CO/N_2	250	ppm	1675b	CO_2/N_2	14.0	percent
1680c	CO/N_2	500	ppm				
1681c	CO/N_2	1000	ppm	1665b	C_3H_8/Air	3	ppm
2637	CO/N_2	2500	ppm	1666b	C_3H_8/Air	10	ppm
2638	CO/N_2	5000	ppm	1667b	C_3H_8/Air	50	ppm
2639	CO/N_2	1	percent	1668b	C_3H_8/Air	100	ppm
2640	CO/N_2	2	percent	1669b	C_3H_8/Air	500	ppm
2641	CO/N_2	4	percent				
2642	CO/N_2	8	percent	2643	C_3H_8/N_2	100	ppm
				2644	C_3H_8/N_2	250	ppm
2657	O_2/N_2	2	percent	2645	C_3H_8/N_2	500	ppm
2658	O_2/N_2	10	percent	2646	C_3H_8/N_2	1000	ppm
2659	O_2/N_2	21	percent	2647	C_3H_8/N_2	2500	ppm
				2648	C_3H_8/N_2	5000	ppm
				2649	C_3H_8/N_2	1	percent
				2650	C_3H_8/N_2	2	percent

NBS-SRM cylinders contain approximately 870 liters of gas at STP.

For availability, contact: Office of Standard Reference Materials
Chemistry Building, Room B311
NBS, Gaithersburg, Maryland 20899
(301) 975-6776. (FTS 879-6776)

4.1 PROCEDURE G1: ASSAY AND CERTIFICATION OF A COMPRESSED GAS STANDARD WITHOUT DILUTION

4.1.1 Applicability

This procedure may be used to assay the concentration of a candidate compressed gas (cylinder) pollutant standard, based on the concentration of a compressed gas (cylinder) reference standard of the same pollutant compound, and certify that the assayed concentration thus established for the candidate standard is traceable to the reference standard. The procedure employs a pollutant gas analyzer to compare the candidate and reference gas concentrations by direct measurement--without dilution of either gas--to minimize assay error.

4.1.2 Limitations

1. The concentration of the candidate gas standard must be between 0.3 and 1.3 times the concentration of the reference gas standard.

2. The analyzer must have a calibrated range capable of directly measuring both the candidate and the reference gas concentrations.

3. The analyzer's response (or transformed response) must be linear with respect to concentration.

4. The balance gas in both the candidate and reference standards must be identical, unless it can be shown that the analyzer is insensitive to any difference in the balance gases.

5. A source of clean, dry zero gas is required.

4.1.3 Assay Apparatus

Figure G1 illustrates the relatively simple assay apparatus. The configuration is designed to allow convenient routing of the zero gas and undiluted samples of the reference gas and candidate gases, in turn, to the analyzer for measurement, as selected by three-way valves V1 and V2. Pressure regulators and needle valves (V3 and V4) control the individual gas flows. The pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess flow and insures that the assay concentrations sampled by the analyzer are always at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. Valves V1 and V2 could be replaced by a single four-way valve (with 3 inputs and 1 output) or by manually moving the output connection to each of the gases as needed. See also subsection 4.0.3.

4.1.4 Analyzer

See subsection 4.0.7.1. The pollutant gas analyzer must have a linear response function and a calibrated range capable of measuring the full concentration of both the candidate and the reference gas standards directly, without dilution. It must

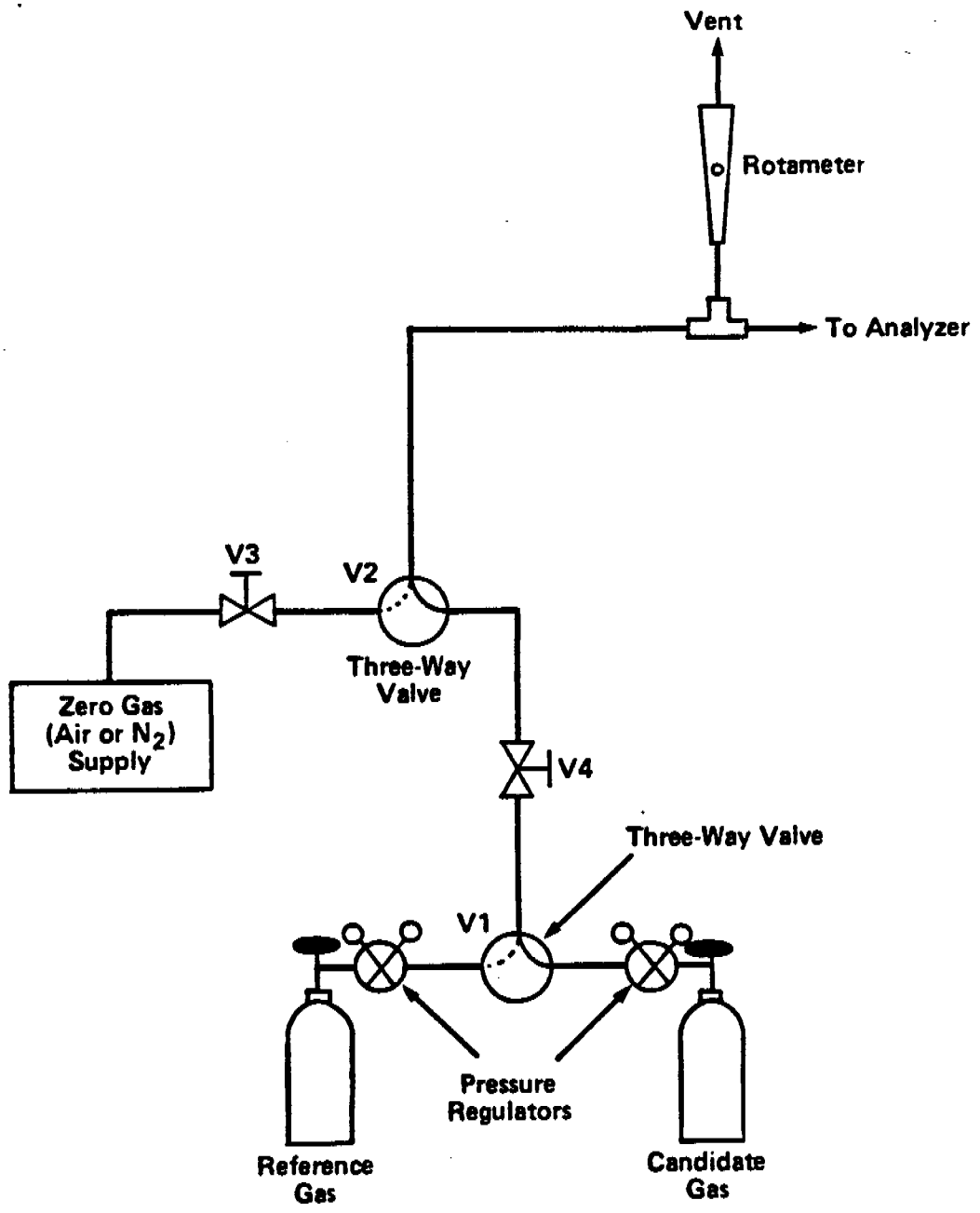


Figure G1. Suggested assay apparatus for Procedure G1.

have good resolution (readability), good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in either the candidate or reference gas. If the candidate and reference gases contain dissimilar balance gases (air versus nitrogen or different proportions of oxygen in the balance air, for example), the analyzer must be proven to be insensitive to the two different balance gases. This may be accomplished by showing no difference in analyzer response when measuring pollutant concentrations diluted with identical flow rates of the two balance gases.

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

4.1.5 Analyzer Calibration

4.1.5.1 Multipoint calibration. See subsections 4.0.7.2 and 4.0.7.4.

4.1.5.2 Calibration range. The calibrated range of the analyzer must include both the candidate and reference gas concentrations, such that the higher concentration does not exceed 97 percent of the upper range limit, and the lower concentration is not below 25 percent of the upper range limit (assuming a lower range limit of zero). Within these limits, select a calibrated analyzer range that will produce the highest analyzer responses.

4.1.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 4.0.7.5). High-concentration-range analyzers of the type that are required for this procedure may not be inherently linear, but they usually have a predictable, non-linear response characteristic that can be mathematically transformed to produce a sufficiently linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve because physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

4.1.5.4 Zero and span adjustment. See subsections 4.0.7.3 and 4.0.7.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to reestablish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero or span adjustment, verify linearity with a multipoint calibration (subsection 4.0.7.2) using at least 3 known pollutant concentrations, including zero.

4.1.6 Assay Gases

4.1.6.1 Candidate gas standard. See subsections 4.0.6 and 4.1.2.

4.1.6.2 Reference gas standard. See subsections 4.0.2, 4.1.2, and 4.0.6.4. Select a reference standard such that the concentration of the candidate gas is not

more than 30 percent above nor less than 70 percent below the concentration of the standard.

4.1.6.3 Zero gas. See subsection 4.0.8. The zero gas should match the balance gas used in the cylinder concentrations.

4.1.7 Assay Procedure

1. Verify that the assay apparatus is properly configured, as described in subsection 4.1.3 and shown in Figure G1.

2. Verify that the linearity of the analyzer has been checked within the last 3 months (see subsections 4.0.7.2, 4.0.7.5, and 4.1.4), that the zero and span are adjusted correctly (subsection 4.0.7.3), that the candidate and reference gas concentrations are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer, and that the analyzer is operating stably.

3. Adjust the flow rates of the three gases (reference, candidate, and zero) to approximately the same value that will provide enough flow for the analyzer and sufficient excess to assure that no ambient air will be drawn into the vent.

4. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the reference gas concentration, and a measurement of the candidate gas concentration. Use valves V1 and V2 to select each of the three concentrations for measurement. For each measurement, allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration and any transformation of the response readings necessary for linearity. Do not translate the response readings to concentration values via the calibration curve (see the footnote following Equation G1). Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.

5. Conduct at least 2 additional measurement triads, similar to step 4 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure reference gas, zero gas, candidate gas for the second triad and zero gas, candidate gas, reference gas for the third triad, etc.).

6. If any one or more of the measurements of a triad is invalid or abnormal for any reason, discard all three measurements of the triad and repeat the triad.

7. For each triad of measurements, calculate the assay concentration of the candidate gas as follows:

$$C_C = C_r \frac{R_C - R_Z}{R_r - R_Z}$$ Equation G1

where: C_c = Assay concentration of the candidate gas standard, ppm or percent;
C_r = Concentration of the reference gas standard, ppm or percent;
R_c = Stable response reading of the analyzer for the candidate gas, analyzer response units;*
R_z = Stable response reading of the analyzer for the zero gas, analyzer response units;*
R_r = Stable response reading of the analyzer for the reference gas, analyzer response units.*

*Analyzer response units are the units used to express the direct response readings of the analyzer, such as volts, millivolts, percent of scale, etc. DO NOT convert these direct response readings to concentration units with the multipoint calibration curve or otherwise adjust these readings except for transformation necessary to achieve response linearity.

8. Calculate the mean of the 3 (or more) valid assays. Calculate the percent difference of each assay from the mean. If any one of the assay values differs from the mean by more than 1.5%, discard that assay value and conduct another triad of measurements to obtain another assay value. When at least 3 assay values all agree within 1.5% of their mean, report the mean value as the certified concentration of the candidate gas standard. For newly-prepared reactive standards, a reassay at least 7 days later is required to check the stability of the standard; see subsection 4.0.6.2.

4.1.8 Stability Test for Newly-Prepared Standards

See subsections 4.0.6.1 and 4.0.6.2.

4.1.9 Certification Documentation

See subsections 4.0.4 and 4.0.5.

4.1.10 Recertification Requirements

See subsections 4.0.6.3 and 4.0.6.4.

4.2 References.

1. Code of Federal Regulations, Title 40, Part 60, "Standards of Performance for New Stationary Sources," Appendix A, Method 20 (1982).

2. Standards of Performance for New Stationary Sources; Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination, promulgated in the Federal Register, June 4, 1987, pp. 21003-21010.

3. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. EPA-600/7-81-010. Joint publication by NBS and EPA, May 1981. Available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory (MD-77), Research Triangle Park, NC 27711.

4. Code of Federal Regulations, Title 40, Part 50, "National Ambient Air Quality Measurement Methodology".

5. Code of Federal Regulations, Title 40, Part 58, "Ambient Air Quality Surveillance," Appendixes A and B.

6. Shores, R. C. and F. Smith, "Stability Evaluation of Sulfur Dioxide, Nitric Oxide, and Carbon Monoxide Gases in Cylinders. NTIS No. PB 85-122646. Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

7. Method 6A and 6B, "Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide Emissions from Fossil Fuel Combustion Sources," Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Section 3.13.8, July 1986. Available from the U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH 45268.

8. "List of Designated Reference and Equivalent Methods." Current edition available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, NC 27711.

2.0.7. PROCEDURES FOR NBS-TRACEABLE CERTIFICATION OF COMPRESSED GAS AND PERMEATION DEVICE WORKING STANDARDS USED FOR CALIBRATION AND AUDIT OF AIR POLLUTION ANALYZERS (Revised Traceability Protocol No. 2)

CONTENTS

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2.0.7.0	General Information	1 to 11
2.0.7.1	Procedure G1: Assay and Certification of a Compressed Gas Standard Without Dilution	G1-1 to G1-5
2.0.7.2	Procedure G2: Assay and Certification of a Compressed Gas Standard Using Dilution	G2-1 to G2-7
2.0.7.3	Procedure P1: Assay and Certification of a Permeation Device Referenced to a Permeation Device Standard	P1-1 to P1-7
2.0.7.4	Procedure P2: Assay and Certification of a Permeation Device Referenced to a Compressed Gas Standard	P2-1 to P2-8
2.0.7.5	References	

7.0 GENERAL INFORMATION

7.0.1 Purpose and Scope of the Procedures

Section 2.0.7 describes procedures for assaying the concentration of gaseous pollutant concentration standards and certifying that the assay concentrations are traceable to an authoritative reference concentration standard. These procedures are recommended for certifying the local working concentration standards required by the pollutant monitoring regulations of 40 CFR Parts 50, 58, and 60[1,2,3,4] for the calibration and audit of air monitoring analyzers. The procedures cover certification of compressed gas (cylinder) standards for CO, CO_2, NO, NO_2, and SO_2 (Procedures G1 and G2) and permeation-type standards for SO_2 and NO_2 (Procedures P1 and P2).

7.0.2 Reference Standards

Parts 50, 58, and 60 of the monitoring regulations[1,2,3,4] require that working standards used for calibration and audit of air monitoring analyzers be traceable to either a National Bureau of Standards (NBS) gaseous Standard Reference Material (SRM) or a NBS/EPA-approved Certified Reference Material (CRM)[5]. Accordingly, the reference standard used for assaying and certifying a working standard for these purposes must be an SRM, a CRM, or a suitable intermediate standard (see the next

paragraph). SRM cylinder gas standards and permeation devices available from NBS are listed in Tables 7.2 and 7.3, respectively, at the end of subsection 7.0. A current list of CRM cylinder gases and CRM vendors is available from the Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U. S. EPA, Research Triangle Park, NC 27711.

The regulations define a "traceable" standard as one which "...has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as a...NBS [gaseous] SRM or...CRM"[1,2]. Certification of a working standard directly to an SRM or CRM primary standard is, of course, preferred and recommended because of the lower error. However, an intermediate reference standard is permitted, if necessary. In particular, a Gas Manufacturer's Intermediate Standard (see subsection 7.0.2.1) that has been referenced directly to an SRM or a CRM according to Procedure G1 is an acceptable intermediate standard and could be used as the reference standard on that basis. However, purchasers of commercial gas standards referenced to an intermediate standard such as a GMIS should be aware that, according to the above definition, such a standard would have to be used directly for calibration or audit. Since a second intermediate standard is not permitted, such a standard could not be used as a reference standard to certify other standards.

7.0.2.1 Gas Manufacturer's Intermediate Standard (GMIS). A GMIS is a compressed (cylinder) gas standard that has been assayed with direct reference to an SRM or CRM and certified according to Procedure G1, and also meets the following requirements:

1. A candidate GMIS must be assayed a minimum of three (3) times, uniformly spaced over a three (3) month period.

2. Each of the three (or more) assays must be within 1.0 percent of the mean of the three (or more) assays.

3. The difference between the last assay and the first assay must not exceed 1.5 percent of the mean of the three (or more) assays.

4. The GMIS must be recertified every three months, and the reassay must be within 1.5 percent of the previous certified assay. The recertified concentration of the GMIS is the mean of the previous certified concentration and the reassay concentration.

7.0.2.2 Recertification of Reference Standards. Recertification requirements for SRMs and CRMs are specified by NBS and NBS/EPA, respectively. See 7.0.2.1 for GMIS recertification requirements.

7.0.3 Selecting a Procedure

The first two procedures (G1 and G2) are applicable to the assay and certification of a candidate compressed gas (cylinder) standard, referenced to a compressed gas (cylinder) reference standard. Procedure G1 provides for assay of the candidate gas concentration by direct, undiluted measurements of both the candidate and reference gases with a pollutant gas analyzer, while procedure G2 allows measurements of diluted gas concentrations. Procedure G1 is preferable because of additional error

introduced by the quantitative dilution technique of procedure G2. However, procedure G1 requires a high-concentration-range gas analyzer capable of accommodating the full concentrations of both the candidate and reference gases, and the procedure also carries a limitation on the difference between the concentrations of the two gases that it can accommodate. The dilution technique of procedure G2 can accommodate a wider range of gas concentrations and uses a low-concentration-range (ambient level) analyzer, but requires a source of clean zero dilution gas and a somewhat more elaborate apparatus.

Procedures P1 and P2 are applicable to the assay and certification of candidate permeation device concentration standards, using an ambient-range gas analyzer. Procedure P1 provides for the assay referenced to a permeation device reference standard, and P2 provides for the assay referenced to a compressed gas (cylinder) reference standard.

7.0.4 Using the Procedures

The assay/certification procedures described here are carefully designed to minimize both systematic and random errors in the assay process. Therefore, the procedures should be carried out as closely as possible to the way they are described. Similarly, the assay apparatus has been specifically designed to minimize errors and should be configured as closely as possible to the design specified. Good laboratory practice should be observed in the selection of inert materials (e.g. Teflon, stainless steel, or glass, if possible) and clean, non-contaminating components for use in portions of the apparatus in contact with the candidate or reference gas concentrations.

7.0.5 Certification Documentation

Each assay/certification must be documented in a written certification report signed by the analyst and containing at least the following information:

1. Identification number (cylinder number or permeation device number).

2. Certified concentration of the standard, in ppm or mole percent for compressed gas standards; or certified permeation rate, in μg/min, and the certification temperature, in degrees C to the nearest 0.1 degree, for permeation device standards.

3. Balance gas in the standard mixture (for compressed gas standards) or the dilution gas (air or nitrogen) used during certification (for permeation device standards).

4. Cylinder pressure at certification (for compressed gas standards).

5. Date of the assay/certification.

6. Certification expiration date (see 7.0.7.3 or 7.0.8.5).

7. Identification of the reference standard used: SRM number, cylinder number, and concentration for an SRM; cylinder number and concentration for a CRM or GMIS; or device number and permeation rate for an NBS permeation device.

8. Statement that the assay/certification was performed according to this Section 2.0.7 and identification of the specific procedure (G1, G2, P1, or P2) used.

9. Identification of the laboratory where the standard was certified and the analyst who performed the certification.

10. Identification of the gas analyzer used for the certification, including the make, model, serial number, the measurement principle, and the date of the last multipoint calibration.

11. Identification of any flowmeters used, their type and scale range, when and by whom they were last calibrated, and the reference standard used for the calibration.

12. All analyzer readings used during the assay/certification and the calculations used to obtain the reported certified value.

13. Chronological record of all certifications for the standard.

Certification concentrations or permeation rates should be reported to 3 significant digits. Certification documentation should be maintained for at least 3 years.

7.0.6 Certification Label

A label or tag bearing the information described in items 1 through 9 of subsection 7.0.5 must be attached to each certified gas cylinder or to the storage container of each certified permeation device.

7.0.7 Assay/Certification of Compressed Gas (Cylinder) Standards

7.0.7.1 Aging of newly-prepared gas standards. Freshly prepared gas standard concentrations and newly filled gas cylinders must be aged before being assayed and certified. SO_2 concentrations contained in steel cylinders must be aged at least 15 days; other standards must be aged at least 4 days.

7.0.7.2 Stability test for reactive gas standards. Reactive gas standards, including nitric oxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and carbon monoxide (CO), that have not been previously certified must be tested for stability as follows: Reassay the concentration at least 7 days after the first assay and compare the two assays. If the second assay differs from the first assay by 1.5% or less, the cylinder may be considered stable, and the mean of the two assays should be reported as the certified concentration. Otherwise, age the cylinder for a week or more and repeat the test, using the second and third assays as if they were the first and second assays. Cylinders that are not stable may not be used for calibration or audit purposes.

7.0.7.3 Recertification of compressed gas standards. Compressed gas standards must be recertified according to this Section 2.0.7 within the time limits specified in Table 7.1[5,6,7]. The reassay concentration must be within 5% of the previous certified concentration. If not, the cylinder must be retested for stability (subsection 7.0.7.2). The certified concentration of a recertified standard

should be reported as the mean of all assays, unless a clear trend or substantial change suggests that previous assays are no longer valid.

Table 7.1 Recertification limits for compressed gas standards.

Pollutant	Balance gas	Concentration range	Maximum months until recertification for cylinder material: Al or SS	other
Carbon monoxide	N_2 or air	≥ 5 ppm	18	6
Nitric oxide	N_2	≥ 10 ppm	18	6
Sulfur dioxide	N_2	≥ 10 ppm	18	6
Nitrogen dioxide	N_2 or air	≥ 10 ppm	6	6
Carbon dioxide	N_2 or air	≥ 300 ppm	18	18
Oxygen	N_2	≥ 2 percent	18	18
Sulfur dioxide and carbon dioxide	N_2	≥ 200 ppm SO_2, ≥ 10 percent CO_2	18	6
Propane	N_2 or air	≥ 5 ppm	18	6
Others not specifically listed			6	6

7.0.7.4 Minimum cylinder pressure. No compressed gas cylinder standard should be used when its gas pressure is below 700 kPa (100 psi), as indicated by the cylinder pressure gauge.

7.0.7.5 Assay/certification of multi-component compressed gas standards. Procedures G1 and G2 may be used to assay and certify individual components of multi-component gas standards, provided that none of the components other than the component being assayed cause a detectable response on the analyzer.

7.0.8 Assay/Certification of Permeation Device Standards

7.0.8.1 Permeation device design. Permeation devices are designed and constructed in various ways, but all devices consist of a sealed chamber containing liquified gas and a permeable area through which the gas is allowed to permeate. The permeated gas is swept and diluted with a measured volumetric flow rate of dry air or nitrogen to create a quantitative concentration of the pollutant gas.

The permeation rate of all permeation devices is critically dependent on temperature; a permeation device is useful as a concentration standard only when its temperature is precisely controlled and accurately measured, and an accurately metered dilution gas flow rate is provided.

7.0.8.2 Precautions for use and storage of permeation devices. The reproducibility of the certified permeation rate of a permeation device may be adversely affected by exposure of the device to temperatures greater than the specified operating or storage temperature range for the device or by exposure to moisture. Permeation devices should be stored under dry conditions and preferably at a temperature between 20 and 25 degrees C, or as otherwise recommended by the manufacturer. Low temperature storage of permeation devices is not recommended.

When stored at a temperature other than the operating or certification temperature, permeation devices require an equilibration period at the operating temperature to reach thermal equilibrium and a stable, accurate permeation rate. When transferred from a different storage temperature, thin-walled permeation devices should be maintained at the operating temperature with a fixed dilution flow rate for at least 24 hours before use or before certification. Other types of permeation devices may require longer equilibration periods. Observe any manufacturer's recommendations for equilibration and use.

7.0.8.3 Aging of newly-prepared permeation devices. A newly-prepared permeation device must be aged at least 48 hours at its operating temperature before being assayed and certified for the first time.

7.0.8.4 Stability test for newly-prepared permeation devices. A permeation device that has not been previously assayed must be tested for stability as follows: Reassay the permeation rate at least 24 hours after the first assay and compare the two assays. If the second assay differs from the first assay by 1.5% or less, the device may be considered stable, and the mean of the two assays should be reported as the certified permeation rate. Otherwise, age the device longer at the operating temperature and repeat the test, using the second and third assays as if they were the first and second. Permeation devices that are not stable may not be used for calibration or audit purposes.

7.0.8.5 Recertification of permeation device standards. Permeation devices should be recertified within 6 months, and more often when they are new and toward the end of their life. A permeation device should also be recertified after temperature excursions beyond its normal or specified storage temperature range, after field excursions where its temperature was not carefully controlled, and after exposure to moisture.

7.0.9 Analyzer Calibration

7.0.9.1 Basic analyzer calibration requirements. The assay procedures described in this Section 2.0.7 employ a direct ratio referencing technique that inherently corrects for minor analyzer calibration variations (drift) and DOES NOT depend on the absolute accuracy of the analyzer calibration. What is required of the analyzer is as follows: 1) it must have a linear response to the pollutant of interest (see subsection 7.0.9.5), 2) it must have good resolution and low noise, 3) its response calibration must be reasonably stable during the assay/certifica-

tion process, and 4) all assay concentration measurements must fall within the calibrated response range of the analyzer.

7.0.9.2 Analyzer multipoint calibration. The gas analyzer used for the assay/certification must have had a multipoint calibration within 3 months of its use for any of these procedures. This calibration is not used to quantitatively interpret analyzer readings during the assay/certification of the candidate gas or permeation device because a more accurate, direct ratio comparison of the candidate concentration to the reference standard concentration is used. However, this multipoint calibration is necessary to establish the calibrated range of the analyzer and its response linearity.

The multipoint calibration should consist of analyzer responses to at least 5 concentrations, including zero, approximately evenly spaced over the concentration range. Analyzer response units may be volts, millivolts, percent of scale, or other measurable analyzer response units. The upper range limit of the calibrated range is determined by the highest calibration point used. If the analyzer has a choice of concentration ranges, the optimum range for the procedure should be selected and calibrated. Plot the calibration points and compute the linear regression slope and intercept. See subsection 7.0.9.5 for linearity requirements and the use of a mathematical transformation, if needed. The intercept should be less than 1 percent of the upper concentration range limit, and the correlation coefficient (r) should be at least 0.999.

7.0.9.3 Zero and span check and adjustment. On each day that the analyzer will be used for assay/certification, its response calibration must be checked with a zero and at least one span concentration near the upper concentration range limit. If necessary, the zero and span controls of the analyzer should be adjusted so that the analyzer's response (i.e. calibration slope) is within about ±5 percent of the response indicated by the most recent multipoint calibration. If a zero or span adjustment is made, allow the analyzer to stabilize for at least an hour or more before beginning the assay procedure, since some analyzers drift for a period of time following zero or span adjustment. If the analyzer is not in continuous operation, turn it on and allow it to stabilize for at least 12 hours before the zero and span check.

7.0.9.4 Pollutant standard for multipoint calibration and zero and span adjustment. The pollutant standard or standards used for multipoint calibration or zero and span checks or adjustments must be obtained from either a compressed gas or permeation device standard certified traceable to an NBS SRM or a NBS/EPA CRM according to one of the procedures of this Section 2.0.7. This standard need not be the same as the reference standard used in the assay/certification. The zero gas must meet the requirements in subsection 7.0.10. If dilution of the standard with zero gas is used, the flow meter or meters used for the dilution should be suitably calibrated with NBS-traceable flow or volume standards and accurate to within 3 percent. Alternatively, the dilution system should be verified by measuring diluted concentrations of a known pollutant concentration standard with an analyzer calibrated independently of the dilution system.

7.0.9.5 Linearity of analyzer response. The direct ratio assay technique used in all four procedures requires that the analyzer have a linear response to concentration. Linearity is determined by comparing the quantitative difference

between a smoothly-drawn calibration curve based on all calibration points and a straight line drawn between zero and an upper reference point (see Figure 1). This difference is measured in concentration units, parallel to the concentration axis, from a point on the calibration curve to the corresponding point for the same response on the straight line.

For the general linearity requirement, the straight line is drawn between zero and the highest calibration point (Figure 1a). Linearity is then acceptable when no point on the smooth calibration curve deviates from the straight line by more than 1.5 percent of the value of the highest calibration concentration. An alternative linearity requirement is defined on the basis of the actual reference and candidate concentrations to be used for the assay. In this case, the reference and candidate concentrations are plotted on the calibration curve, and the straight line is drawn from zero to the reference concentration and extrapolated, if necessary, beyond the candidate concentration (Figure 1b). The deviation of the smooth calibration curve from the straight line at the candidate concentration point then must not exceed 0.8 percent of the value of the reference concentration. This latter specification may allow the use of an analyzer having greater nonlinearity when the reference and candidate concentrations are nearly the same.

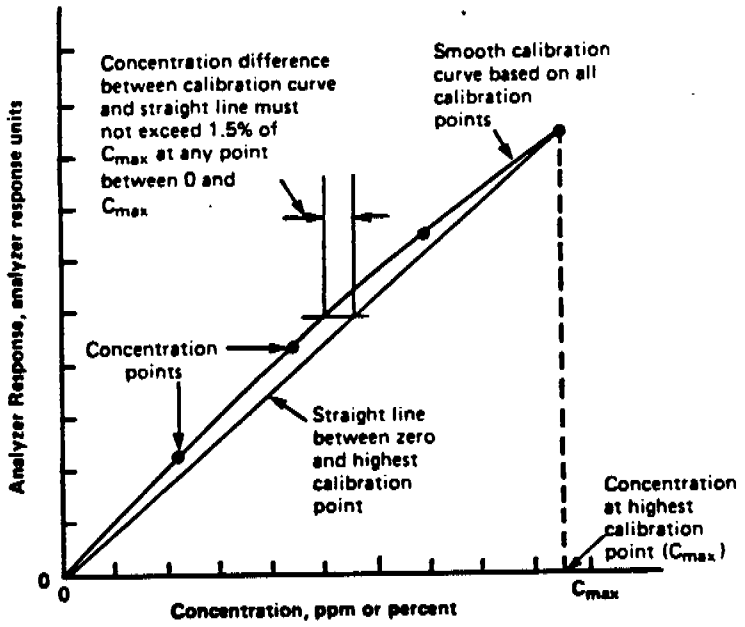
For analyzers having an inherently non-linear response, the response can usually be linearized with a simple mathematical transformation of the response values, such as R'= square root(R) or R'= log(R), where R' is the transformed response value and R is the actual analyzer response value. Using the transformed response values, the multipoint calibration should meet one of the above linearity requirements as well as the requirements for intercept and correlation coefficient given in subsection 7.0.9.2.

7.0.10 Zero Gas

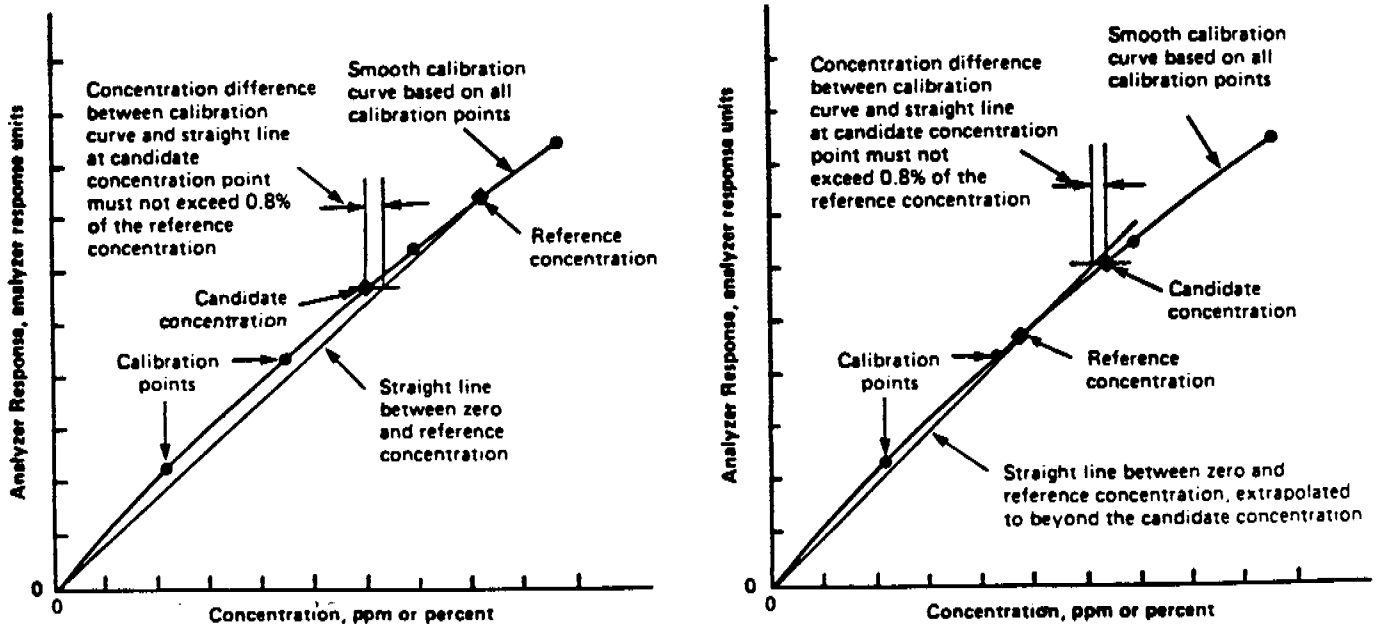
Zero gas used for dilution of any candidate or reference standard should be clean, dry, zero-grade air or nitrogen containing a concentration of the pollutant of interest equivalent to less than 0.5 percent of the analyzer's upper range limit concentration. The zero gas also should contain no contaminant that causes a detectable response on the analyzer or that suppresses or enhances the analyzer's response to the pollutant. The oxygen content of zero air should be the same as that of ambient air.

7.0.11 Accuracy Assessment of Commercially Available Standards

Periodically, the USEPA will assess the accuracy of commercially available compressed gas and permeation device standards that have been assayed and certified according to one of the procedures of this Section 2.0.7. Accuracy will be assessed by EPA audit analysis of representative actual commercial standards obtained via an anonymous agent. The accuracy audit results, identifying the actual gas manufacturers or vendors, will be published as public information.



a) General linearity requirement



b) Alternative linearity requirement

Figure 1. Illustration of linearity requirements.

Table 7.2. NBS SRM reference gases.

SRM number	Type	Nominal concentration		SRM number	Type	Nominal concentration	
2627	NO/N_2	5	ppm	1693	SO_2/N_2	50	ppm
2628	NO/N_2	10	ppm	1694	SO_2/N_2	100	ppm
2629	NO/N_2	20	ppm	1661a	SO_2/N_2	500	ppm
1683b	NO/N_2	50	ppm	1662a	SO_2/N_2	1000	ppm
1684b	NO/N_2	100	ppm	1663a	SO_2/N_2	1500	ppm
1685b	NO/N_2	250	ppm	1664a	SO_2/N_2	2500	ppm
1686b	NO/N_2	500	ppm	1696	SO_2/N_2	3500	ppm
1687b	NO/N_2	1000	ppm				
2630	NO/N_2	1500	ppm	1670	CO_2/Air	330	ppm
2631	NO/N_2	3000	ppm	1671	CO_2/Air	340	ppm
				1672	CO_2/Air	350	ppm
2653	NO_2/Air	250	ppm				
2654	NO_2/Air	500	ppm	2632	CO_2/N_2	300	ppm
2655	NO_2/Air	1000	ppm	2633	CO_2/N_2	400	ppm
2656	NO_2/Air	2500	ppm	2634	CO_2/N_2	800	ppm
				2619a	CO_2/N_2	0.5	percent
2612a	CO/Air	10	ppm	2620a	CO_2/N_2	1.0	percent
2613a	CO/Air	20	ppm	2621a	CO_2/N_2	1.5	percent
2614a	CO/Air	45	ppm	2622a	CO_2/N_2	2.0	percent
				2623a	CO_2/N_2	2.5	percent
1677c	CO/N_2	10	ppm	2624a	CO_2/N_2	3.0	percent
2635	CO/N_2	25	ppm	2625a	CO_2/N_2	3.5	percent
1678c	CO/N_2	50	ppm	2626a	CO_2/N_2	4.0	percent
1679c	CO/N_2	100	ppm	1674b	CO_2/N_2	7.0	percent
2636	CO/N_2	250	ppm	1675b	CO_2/N_2	14.0	percent
1680c	CO/N_2	500	ppm				
1681c	CO/N_2	1000	ppm	1665b	C_3H_8/Air	3	ppm
2637	CO/N_2	2500	ppm	1666b	C_3H_8/Air	10	ppm
2638	CO/N_2	5000	ppm	1667b	C_3H_8/Air	50	ppm
2639	CO/N_2	1	percent	1668b	C_3H_8/Air	100	ppm
2640	CO/N_2	2	percent	1669b	C_3H_8/Air	500	ppm
2641	CO/N_2	4	percent				
2642	CO/N_2	8	percent	2643	C_3H_8/N_2	100	ppm
				2644	C_3H_8/N_2	250	ppm
2657	O_2/N_2	2	percent	2645	C_3H_8/N_2	500	ppm
2658	O_2/N_2	10	percent	2646	C_3H_8/N_2	1000	ppm
2659	O_2/N_2	21	percent	2647	C_3H_8/N_2	2500	ppm
				2648	C_3H_8/N_2	5000	ppm
				2649	C_3H_8/N_2	1	percent
				2650	C_3H_8/N_2	2	percent

NBS-SRM cylinders contain approximately 870 liters of gas at STP.

For availability, contact: Office of Standard Reference Materials
Chemistry Building, Room B311
NBS, Gaithersburg, Maryland 20899
(301) 975-6776. (FTS 879-6776)

Table 7.3. NBS SRM permeation device reference standards.

SRM	Type	Device length, cm	Nominal permeation rate, µg/min at 25 °C	Typical concentration, ppm at flow rates of 1 L/min	5 L/min
1625	Sulfur dioxide	10	2.8	1.07	0.214
1626	Sulfur dioxide	5	1.4	0.535	0.107
1627	Sulfur dioxide	2	0.56	0.214	0.0428
1629a	Nitrogen dioxide	10	1.0	0.5	0.1

For availability, see the address at the bottom of Table 7.2.

7.1 PROCEDURE G1: ASSAY AND CERTIFICATION OF A COMPRESSED GAS STANDARD WITHOUT DILUTION

7.1.1 Applicability

This procedure may be used to assay the concentration of a candidate compressed gas (cylinder) pollutant standard, based on the concentration of a compressed gas (cylinder) reference standard of the same pollutant compound, and certify that the assayed concentration thus established for the candidate standard is traceable to the reference standard. The procedure employs a pollutant gas analyzer to compare the candidate and reference gas concentrations by direct measurement--without dilution of either gas--to minimize assay error. For this reason, this procedure is preferable to Procedure G2, which employs quantitative dilution of the gas concentrations.

7.1.2 Limitations

1. The concentration of the candidate gas standard must be between 0.3 and 1.3 times the concentration of the reference gas standard.

2. The analyzer must have a calibrated range capable of directly measuring both the candidate and the reference gas concentrations.

3. The analyzer's response (or transformed response) must be linear with respect to concentration.

4. The balance gas in both the candidate and reference standards must be identical, unless it can be shown that the analyzer is insensitive to any difference in the balance gases.

5. A source of clean, dry zero gas is required.

7.1.3 Assay Apparatus

Figure G1 illustrates the relatively simple assay apparatus. The configuration is designed to allow convenient routing of the zero gas and undiluted samples of the reference gas and candidate gases, in turn, to the analyzer for measurement, as selected by three-way valves V1 and V2. Pressure regulators and needle valves (V3 and V4) control the individual gas flows. The pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess flow and insures that the assay concentrations sampled by the analyzer are always at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. Valves V1 and V2 could be replaced by a single four-way valve (with 3 inputs and 1 output) or by manually moving the output connection to each of the gases as needed. See also subsection 7.0.4.

7.1.4 Analyzer

See subsection 7.0.9.1. The pollutant gas analyzer must have a linear response

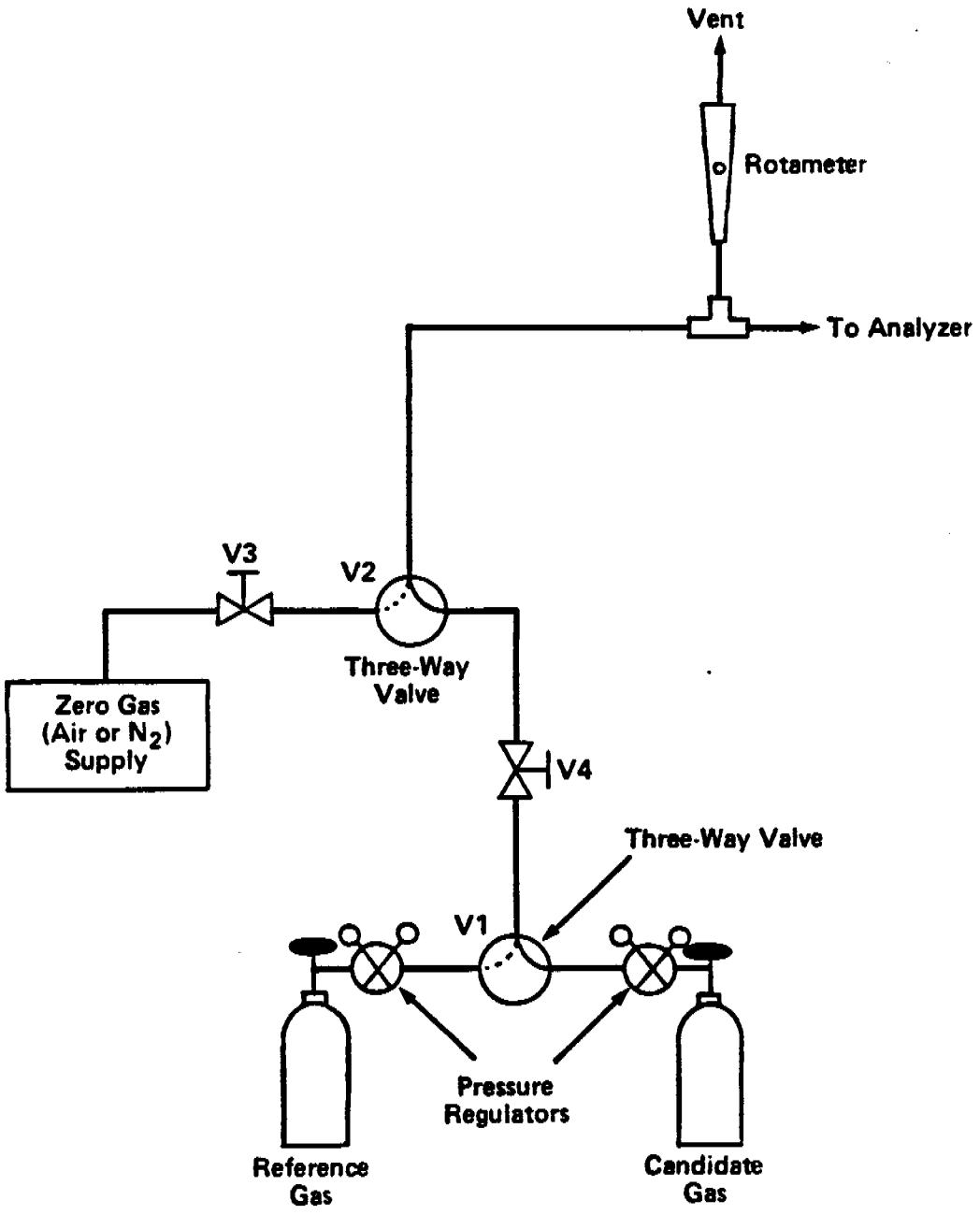


Figure G1. Suggested assay apparatus for Procedure G1.

function and a calibrated range capable of measuring the full concentration of both the candidate and the reference gas standards directly, without dilution. It must have good resolution (readability), good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in either the candidate or reference gas. If the candidate and reference gases contain dissimilar balance gases (air versus nitrogen or different proportions of oxygen in the balance air, for example), the analyzer must be proven to be insensitive to the two different balance gases. This may be accomplished by showing no difference in analyzer response when measuring pollutant concentrations diluted with identical flow rates of the two balance gases.

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

7.1.5 Analyzer Calibration

7.1.5.1 Multipoint calibration. See subsections 7.0.9.2 and 7.0.9.4.

7.1.5.2 Calibration range. The calibrated range of the analyzer must include both the candidate and reference gas concentrations, such that the higher concentration does not exceed 97 percent of the upper range limit, and the lower concentration is not below 25 percent of the upper range limit (assuming a lower range limit of zero). Within these limits, select a calibrated analyzer range that will produce the highest analyzer responses.

7.1.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 7.0.9.5). High-concentration-range analyzers of the type that are required for this procedure may not be inherently linear, but they usually have a predictable, non-linear response characteristic that can be mathematically transformed to produce a sufficiently linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve because physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

7.1.5.4 Zero and span adjustment. See subsections 7.0.9.3 and 7.0.9.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to reestablish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero or span adjustment, verify linearity with a multipoint calibration (subsection 7.0.9.2) using at least 3 known pollutant concentrations, including zero.

7.1.6 Assay Gases

7.1.6.1 Candidate gas standard. See subsections 7.0.7 and 7.1.2.

7.1.6.2 Reference gas standard. See subsections 7.0.2, 7.1.2, and 7.0.7.4. Select a reference standard such that the concentration of the candidate gas is not more than 30 percent above nor less than 70 percent below the concentration of the standard.

7.1.6.3 Zero gas. See subsection 7.0.10. The zero gas should match the balance gas used in the cylinder concentrations.

7.1.7 Assay Procedure

1. Verify that the assay apparatus is properly configured, as described in subsection 7.1.3 and shown in Figure G1.

2. Verify that the linearity of the analyzer has been checked within the last 3 months (see subsections 7.0.9.2, 7.0.9.5, and 7.1.4), that the zero and span are adjusted correctly (subsection 7.0.9.3), that the candidate and reference gas concentrations are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer, and that the analyzer is operating stably.

3. Adjust the flow rates of the three gases (reference, candidate, and zero) to approximately the same value that will provide enough flow for the analyzer and sufficient excess to assure that no ambient air will be drawn into the vent.

4. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the reference gas concentration, and a measurement of the candidate gas concentration. Use valves V1 and V2 to select each of the three concentrations for measurement. For each measurement, allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration and any transformation of the response readings necessary for linearity. Do not translate the response readings to concentration values via the calibration curve (see the footnote following Equation G1). Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.

5. Conduct at least 2 additional measurement triads, similar to step 4 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure reference gas, zero gas, candidate gas for the second triad and zero gas, candidate gas, reference gas for the third triad, etc.).

6. If any one or more of the measurements of a triad is invalid or abnormal for any reason, discard all three measurements of the triad and repeat the triad.

7. For each triad of measurements, calculate the assay concentration of the candidate gas as follows:

$$C_C = C_r \frac{R_C - R_Z}{R_r - R_Z} \qquad \text{Equation G1}$$

where: C_c = Assay concentration of the candidate gas standard, ppm or percent;
C_r = Concentration of the reference gas standard, ppm or percent;
R_c = Stable response reading of the analyzer for the candidate gas, analyzer response units;*
R_z = Stable response reading of the analyzer for the zero gas, analyzer response units;*
R_r = Stable response reading of the analyzer for the reference gas, analyzer response units.*

*Analyzer response units are the units used to express the direct response readings of the analyzer, such as volts, millivolts, percent of scale, etc. DO NOT convert these direct response readings to concentration units with the multipoint calibration curve or otherwise adjust these readings except for transformation necessary to achieve response linearity.

8. Calculate the mean of the 3 (or more) valid assays. Calculate the percent difference of each assay from the mean. If any one of the assay values differs from the mean by more than 1.5%, discard that assay value and conduct another triad of measurements to obtain another assay value. When at least 3 assay values all agree within 1.5% of their mean, report the mean value as the certified concentration of the candidate gas standard. For newly-prepared reactive standards, a reassay at least 7 days later is required to check the stability of the standard; see subsection 7.0.7.2.

7.1.8 Stability Test for Newly-Prepared Standards

See subsections 7.0.7.1 and 7.0.7.2.

7.1.9 Certification Documentation

See subsections 7.0.5 and 7.0.6.

7.1.10 Recertification Requirements

See subsections 7.0.7.3 and 7.0.7.4.

7.2 PROCEDURE G2: ASSAY AND CERTIFICATION OF A COMPRESSED GAS STANDARD USING DILUTION

7.2.1 Applicability

This procedure may be used to assay the concentration of a candidate compressed gas (cylinder) pollutant standard, based on the concentration of a compressed gas (cylinder) reference standard of the same pollutant compound, and certify that the assayed concentration thus established for the candidate standard is traceable to the reference standard. The procedure employs a low-concentration-range (ambient level) pollutant gas analyzer to compare quantitatively diluted concentrations of both the candidate and reference gases. Dilution of the original gas cylinder concentrations with zero gas allows greater flexibility in the range of cylinder concentrations of both the candidate and reference gases that can be accommodated and also allows the use of a low-concentration-range analyzer, which is more likely to have an inherently linear response. However, the dilution technique introduces additional error into the assay. For this reason, this procedure should be used only when Procedure G1 cannot be used.

7.2.2 Limitations

1. The analyzer's response (or transformed response) must be linear with respect to concentration (see subsection 7.2.5.3).

2. A quantitatively accurate flow measurement and dilution system is required.

3. A source of clean, dry, zero gas is required.

4. The balance gas in both the candidate and reference standards must be identical, unless either a high dilution ratio (at least 50:1) is used or it can be shown that the analyzer is insensitive to any difference in the balance gases.

7.2.3 Assay Apparatus

Figure G2 illustrates the components and configuration of the assay apparatus, including a common dilution system for both the reference and candidate gases. The configuration is designed to allow convenient routing of zero gas and diluted concentrations of the reference and candidate gases, in turn, to the analyzer for measurement, as selected by valves V1 and V2. One flow controller controls the flow rates of the candidate and reference gas flows, which are measured by a single, common flow meter. Another flow controller and flow meter controls and measures the zero gas dilution flow. The flow controllers may be needle valves, pressure regulators, electronic flow controllers, or other means of flow control. If different dilution flow rates are used for the candidate and reference gases (see subsection 7.2.6), separate flow controllers may also be used for these two gas flows, if desired; however, the same flow meter should always be used to measure these two flow rates to minimize systematic (proportional) flow measurement errors (see also subsection 7.2.7). Flow rates should be controlled to within 1 percent variation during the assay. At high dilution ratios, the candidate and reference gas flow rates may be quite low. Therefore, the internal volumes of the lines and flow components

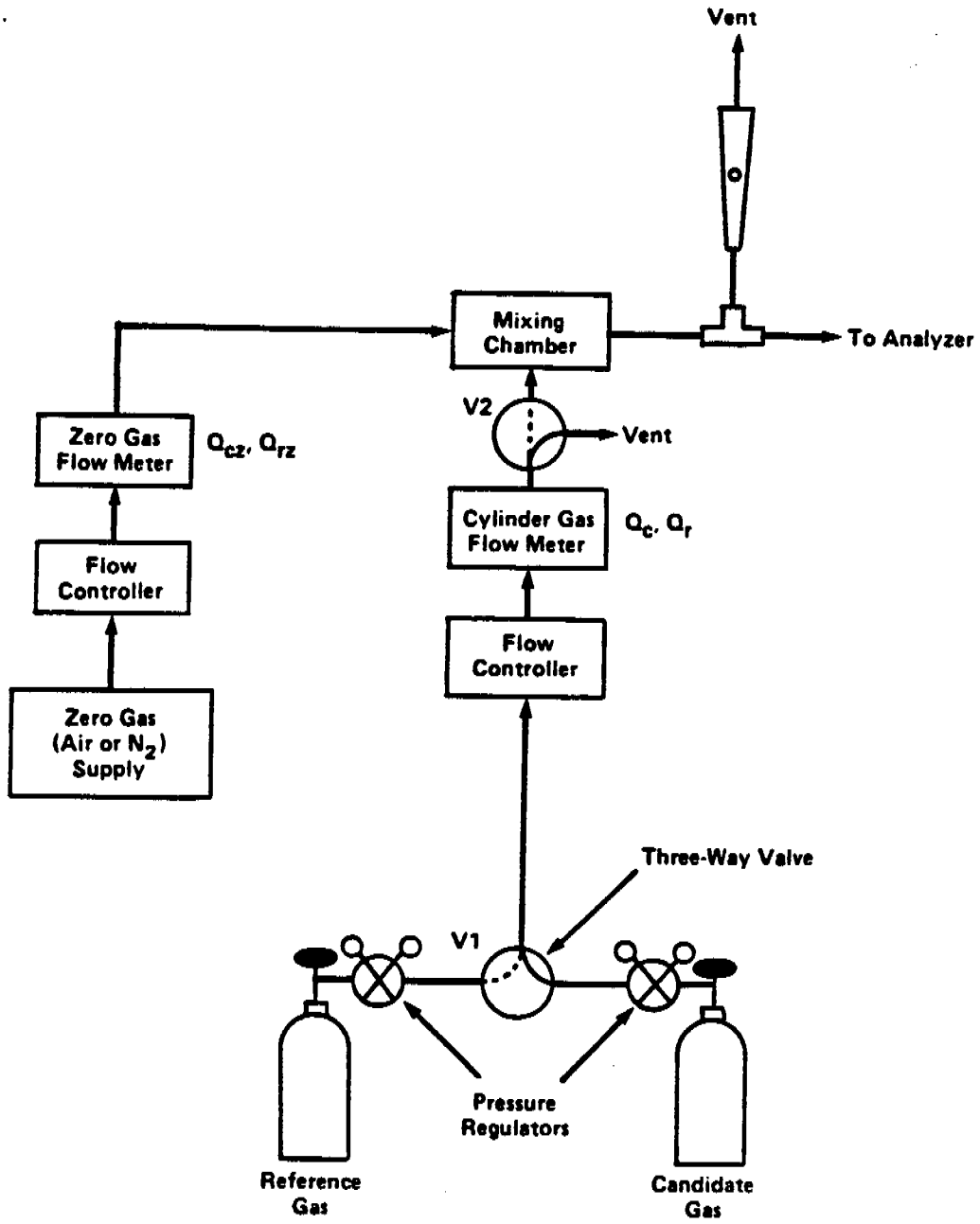


Figure G2. Suggested assay apparatus for Procedure G2.

for these flows should be minimized to reduce the flush time required when valve V1 is switched.

The mixing chamber combines the gas flows and should be designed to provide turbulence in the flow to insure thorough mixing of the two gas streams. The diluted pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess gas flow and insures that the assay concentrations sampled by the analyzer are at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. Valves V1 and V2 could be replaced by manually moving the connections as needed. See also subsection 7.0.4. Check the apparatus carefully for leaks and correct all leaks before use.

7.2.4 Analyzer

See subsection 7.0.9.1. The pollutant gas analyzer must have a linear response function and a calibrated range capable of measuring the diluted concentration of both the candidate and the reference gas standards. It must have good resolution (readability), good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in either the candidate or reference gas. A suitable analyzer may be selected from the list of EPA-designated reference and equivalent method analyzers[8]. If the candidate and reference gases contain dissimilar balance gases (air versus nitrogen or different proportions of oxygen in the balance air, for example, either a high dilution ratio (> 50:1) should be used or the analyzer must be proven to be insensitive to the two different gases. The latter may be accomplished by showing no difference in analyzer response when measuring pollutant concentrations diluted with identical flow rates of the two balance gases.

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

7.2.5. Analyzer Calibration

7.2.5.1 Multipoint calibration. See subsections 7.0.9.2 and 7.0.9.4.

7.2.5.2 Calibration range. The calibrated range of the analyzer must include the diluted concentrations of both the candidate and reference gases (see subsection 7.2.6). The higher concentration should not exceed 97 percent of the upper range limit, and the lower concentration should not be less than 25 percent of the upper range limit (assuming a lower range limit of zero). Since the selection of the dilution ratio or ratios used provides great flexibility in the choice of concentrations to be measured by the analyzer, the analyzer range should be selected based on optimum accuracy, stability, and linearity.

7.2.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 7.0.9.5). Many low-range analyzers of the type that may be used for this procedure are sufficiently linear. If not, they usually have a predictable nonlinear response characteristic that can be mathematically transformed to produce

a linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve because physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

7.2.5.4 Zero and span adjustment. See subsection 7.0.9.3 and 7.0.9.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to reestablish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero or span adjustment, verify linearity with a multipoint calibration (subsection 7.0.9.2) using at least 3 known pollutant concentrations, including zero.

7.2.6 Selection of Gas Dilution Flow Rates

The dilution flow rates used for the reference, candidate, and zero gases should be selected carefully, in conjunction with selection of the analyzer range, to provide diluted concentrations for both the candidate and reference gases that fall preferably in the upper half of the measurement range of the analyzer, and in any case, between 25 and 97 percent of the upper range limit. Potential assay error due to the dilution process will be greatly reduced if exactly the same dilution flow rate ratio can be used for both the candidate and reference gases. This is feasible if the concentration of the candidate gas is between 0.3 and 1.3 times the concentration of the reference gas. Thus, if at all possible, select the concentrations of the reference and candidate gases to meet those limits, and determine the pollutant and zero gas flow rates that will produce the highest analyzer responses within the analyzer's measurement range for both the reference and candidate gases.

If the same dilution ratio cannot be used for both the candidate and reference gases, select different flow rate ratios for the candidate and reference gases to provide approximately equal diluted concentrations that fall in the upper half of the analyzer's measurement range. Where possible, select flow rates such that only one of the flow controllers must be adjusted when switching from the reference gas to the candidate gas, or vice versa. Where a choice of analyzer ranges is available, higher dilution ratios will tend to reduce the consumption of the standard gases and reduce any error from dissimilar balance gases in the two standards.

7.2.7 Flow Meter Type and Flow Meter Calibration

The flow meters, as shown in Figure G2, measure in-line flow rates and may not operate at atmospheric pressure because of backpressure from downstream components. Also, this backpressure is variable, depending on the total flow rate. Thus, the flowmeters must be of non-contaminating design and must compensate for the variable in-line pressure. For this reason, mass-type flow meters are recommended. Measurements from pressure-sensitive flowmeters such as rotameters or volume meters must be carefully corrected for the actual meter pressure during the flow measurement. A non-venting pressure regulator may be inserted downstream of the flowmeter so that the flowmeter operates at a fixed pressure regardless of the total flow rate.

Alternatively, the flow rates can be measured at the outlet of the dilution

apparatus, with the vent temporarily plugged. In this case, a volume-type meter such as a wet test meter or a bubble meter can be used, and flow measurements may be conveniently referenced to atmospheric pressure. However, each flow rate must be measured independently, in turn, while the other flow rates are set to zero. Accordingly, great care must be exercised to insure that each measured flow rate remains constant when combined with the other flow rate(s) and between the time of measurement and the time of the assay.

The flow meters used should be stable, repeatable, linear, and have good resolution (readability). If possible, select flow rates or a flow meter range such that the flow rates to be measured fall in the upper half of the flow meter's range. The flow meters should be carefully calibrated at several flow rates to prove linearity. The calibration should be accurate to ±2 percent, referenced to an accurate flow or volume standard traceable to an NBS primary standard. Flow meter calibrations should be checked and recertified periodically, as determined by stability information such as a chronological control chart of calibration stability. All volumetric flow rate measurements must be corrected or referenced to the same temperature and pressure conditions, such as EPA-standard conditions (760 mm Hg, 25 degrees C) or the ambient temperature and pressure conditions prevailing in the laboratory during the assay.

Measurement of both cylinder gas flow rates with the same flow meter, and measurement of both dilution zero gas flow rates with the same flow meter, tend to reduce systematic (proportional) flow measurement error, especially at higher dilution ratios and if the flow meters are linear (see Equation G2). Note particularly that flow measurement error is greatly reduced if the same dilution ratio can be used for both the reference and candidate gases.

7.2.8 Assay Gases

7.2.8.1 Candidate gas standard. See subsections 7.0.7, 7.2.2, and 7.2.6.

7.2.8.2 Reference gas standard. See subsections 7.0.2, 7.0.7.4, 7.2.2, and 7.2.6.

7.2.8.3 Zero gas. See subsection 7.0.10. Use the same zero gas for dilution of both candidate and reference gases.

7.2.9 Assay Procedure

1. Verify that the assay apparatus is properly configured as shown in Figure G2 and described in subsection 7.2.3.

2. Verify that the flow meters are properly calibrated (subsection 7.2.7).

3. Verify that the linearity of the analyzer has been checked within the last 3 months (see subsections 7.0.9.2, 7.0.9.5, and 7.2.4), that the zero and span are adjusted correctly (subsection 7.0.9.3), and that the analyzer is operating stably.

4. Determine and establish the flow rates of the three gases (reference, candidate, and zero) that will be used for the assay (see subsections 7.2.6, 7.2.7, and 7.2.5.2). Ensure that the diluted candidate and reference gas concentrations

are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer. Also check that both the candidate and reference dilution flow rates will provide enough flow for the analyzer, with sufficient excess to assure that no ambient air will be drawn into the vent, and without increasing the pressure of the sample delivered to the analyzer. When using the same dilution ratios for both candidate and reference gases, carefully set the delivery pressures of the two gases to the same value so that there is no change in the flow rate when switching from one gas to the other.

5. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the diluted reference gas concentration, and a measurement of the diluted candidate gas concentration. Use valves V1 and V2 to select each of the three concentrations for measurement. For each measurement, adjust the flow rates, if necessary, to those determined in step 4, and allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration (and any transformation of the response readings necessary for analyzer linearity). Do not translate or adjust the response readings via the calibration curve. Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.

6. Conduct at least 2 additional measurement triads, similar to step 5 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure reference gas, zero gas, candidate gas for the second triad and zero gas, candidate gas, reference gas for the third triad, etc.).

7. If any one or more of the measurements of a triad is invalid or abnormal for any reason, discard all three measurements of the triad and repeat the triad.

8. For each triad of measurement, calculate the assay concentration of the candidate gas as follows:

$$C_C = C_r \frac{Q_{cz} + Q_c}{Q_c} \frac{Q_r}{Q_{rz} + Q_r} \frac{R_C - R_Z}{R_r - R_Z} \qquad \text{Equation G2}$$

where: C_C = Assay concentration of the undiluted candidate gas standard, ppm or percent;
C_r = Concentration of the undiluted reference gas standard, ppm or percent;
Q_{cz} = Flow rate of the zero gas for the candidate gas dilution, cm^3/min;*
Q_c = Flow rate of the (undiluted) candidate gas for the candidate gas dilution, cm^3/min;*
Q_r = Flow rate of the (undiluted) reference gas for the reference gas dilution, cm^3/min;*
Q_{rz} = Flow rate of the zero gas for the reference gas dilution, cm^3/min;*
R_C = Stable response reading of the analyzer to the diluted candidate gas concentration, analyzer response units;**

R_z = Stable response reading of the analyzer to the zero gas, analyzer response units;**
R_r = Stable response reading of the analyzer to the diluted reference gas concentration, analyzer response units.**

*Flow measurement units must be equivalent; it is suggested that all flow rate measurements be corrected either to EPA standard conditions of 25 degrees C and 760 mm Hg or to the temperature and pressure prevailing in the laboratory during the assay.

**Analyzer response units are the units used to express the direct response readings of the analyzer, such as volts, millivolts, percent of scale, etc. DO NOT convert these direct response readings to concentration units with the calibration curve or otherwise adjust these readings except for transformation necessary to achieve response linearity.

Note that when the same dilution ratio is used for both the candidate and reference gases, $Q_{cz} = Q_{rz}$, $Q_c = Q_r$, and the flow rate measurement terms in Equation G2 cancel.

9. Calculate the mean of the 3 (or more) valid assays. Calculate the percent difference of each assay from the mean. If any one of the assay values differs from the mean by more than 1.5%, discard that assay value and conduct another triad of measurements to obtain another assay value. When at least 3 assay values all agree within 1.5% of their mean, report the mean value as the certified concentration of the candidate gas standard. For newly-prepared reactive standards, a reassay after at least 7 days is required to check the stability of the gas; see subsection 7.0.7.2.

7.2.10 Stability Test for Newly-Prepared Standards

See subsections 7.0.7.1 and 7.0.7.2.

7.2.11 Certification Documentation

See subsections 7.0.5 and 7.0.6.

7.2.12 Recertification Requirements

See subsection 7.0.7.3 and 7.0.7.4.

7.3 PROCEDURE P1: ASSAY AND CERTIFICATION OF A PERMEATION DEVICE REFERENCED TO A PERMEATION DEVICE STANDARD

7.3.1 Applicability

This procedure may be used to assay the permeation rate of a candidate SO_2 or NO_2 permeation device pollutant standard, based on the permeation rate of a permeation device reference standard of the same pollutant compound, and certify that the assayed permeation rate thus established for the candidate standard is traceable to the reference standard. The procedure employs a low-concentration range (ambient level) pollutant gas analyzer to compare quantitatively diluted concentrations from the two permeation devices for the assay of the candidate device.

7.3.2 Limitations

1. The analyzer's response (or transformed response) must be linear with respect to concentration.

2. A quantitatively accurate flow measurement and dilution system is required.

3. A source of clean, dry zero gas is required.

4. This procedure is designed to assay the absolute permeation rate of a candidate permeation device, using a specially designed external assay dilution system; the procedure does not accommodate the certification of a candidate permeation device standard together with its own self-contained dilution/flow measurement system.

7.3.3 Assay Apparatus

Figure P1 illustrates the components and configuration of the assay apparatus, including a common dilution system for both the reference and candidate permeation devices. The configuration is designed to allow convenient routing of zero gas and diluted concentrations of the reference and candidate permeation devices, in turn, to the analyzer for measurement, as selected by valves V1, V2, and V3. One flow controller controls the total dilution flow rates for both the candidate and reference permeation devices, and these flow rates are measured by a single, common (primary) flow meter. The flow controller may be a needle valve, pressure regulator, electronic flow controller, or other means of flow control. Flow rates should be controlled to within 1 percent variation during the assay.

Valve V6 forces a portion (usually 10 to 500 cm^3/min) of the total dilution flow through one or the other of the two temperature-controlled permeation device containers, as selected by valves V1 and V2, to sweep up the permeated pollutant gas. This sweep flow rate is monitored by an auxiliary flow meter for each permeation device. These auxiliary flow meters need not be accurately calibrated, since only the total dilution flow (Q_C for the candidate device and Q_R for the reference device) measured by the primary flow meter is used in the dilution calculation. Optional valves V4 and V5 can be used to individually adjust and balance the two sweep flow rates, if necessary, although these valves may not be needed in addition to the flow controller. The non-selected permeation device receives an approxi-

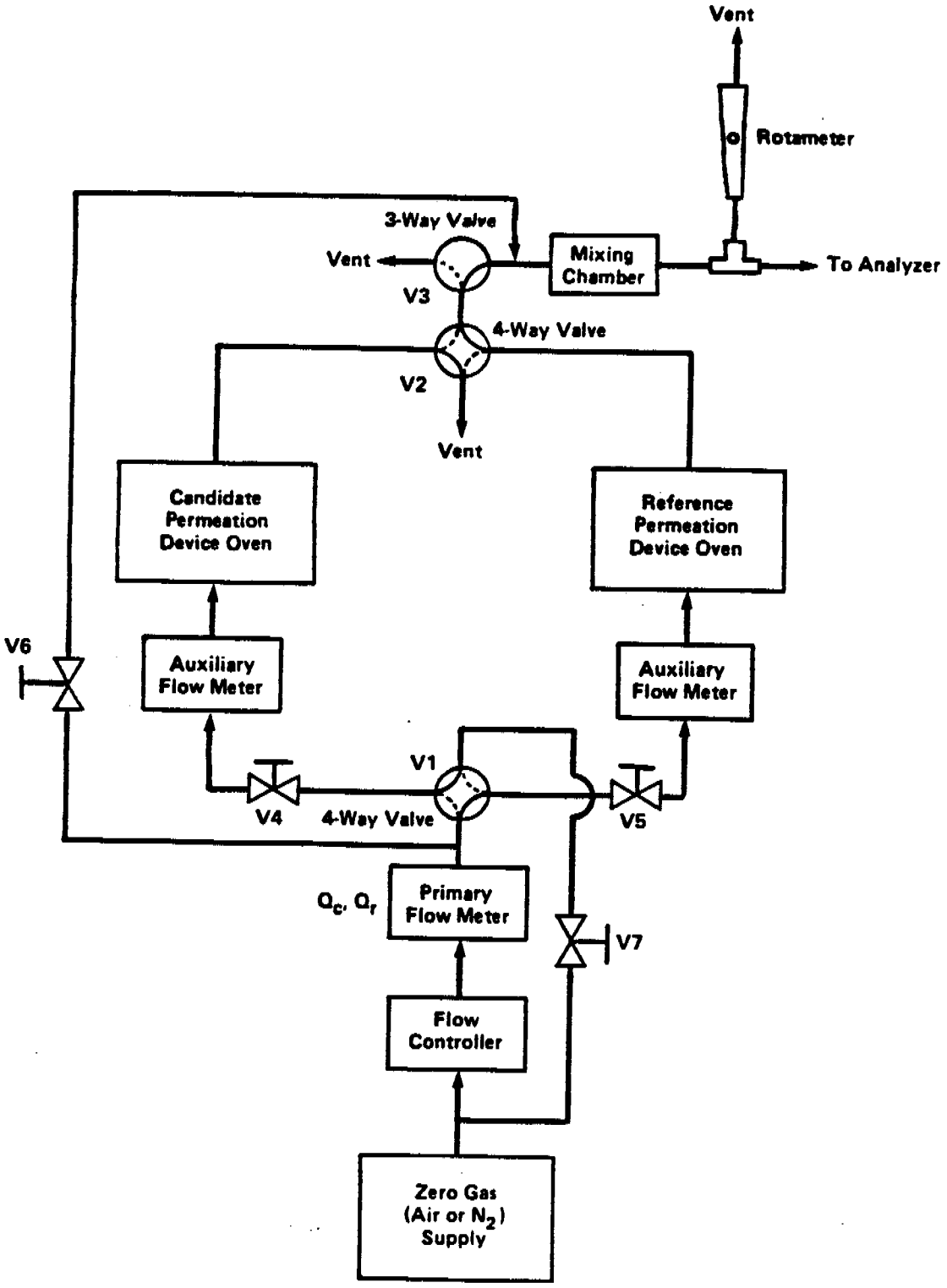


Figure P1. Suggested assay apparatus for Procedure P1.

mately equivalent zero gas purge flow rate, controlled by valve V7, to avoid a high pollutant concentration accumulation during periods when it is not in use. This purge flow is vented by valve V2, and is not measured by the primary flow meter.

If it is necessary to use different dilution flow rates for the candidate and reference permeation devices (see subsection 7.3.6), separate flow controllers for the two permeation devices may be used for the two different flows, if desired; however, the same flow meter should always be used to measure these two flow rates to minimize systematic (proportional) flow measurement errors.

The mixing chamber combines the gas flows and should be designed to provide turbulence in the flow to insure thorough mixing of the two gas streams. The diluted pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess flow and insures that the assay concentrations sampled by the analyzer are at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. See also subsection 7.0.4. Check the apparatus carefully for leaks and correct all leaks before use.

7.3.4 Analyzer

See subsection 7.0.9.1. The pollutant gas analyzer must have a linear response function and a calibrated range capable of measuring the diluted concentrations of both the candidate and the reference permeation devices. It must have good resolution (readability), good precision, a stable response, and low output signal noise. A suitable analyzer may be selected from the list of EPA-designated reference and equivalent method analyzers[8].

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

7.3.5. Analyzer Calibration

7.3.5.1 Multipoint calibration. See subsections 7.0.9.2 and 7.0.9.4.

7.3.5.2 Calibration range. The calibrated range of the analyzer must include the diluted concentrations of both the candidate and reference permeation devices (see subsections 7.3.6). The higher concentration should not exceed 97 percent of the upper range limit, and the lower concentration should not be less than 25 percent of the upper range limit (assuming a lower range limit of zero). Since the selection of the dilution ratio or ratios used provides great flexibility in the choice of concentrations to be measured by the analyzer, the analyzer range should be selected based on optimum accuracy, stability, and linearity.

7.3.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 7.0.9.5). Many low-range analyzers of the type that may be used for this procedure are sufficiently linear. If not, they usually have a predictable nonlinear response characteristic that can be mathematically transformed to produce a linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve be-

cause physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

7.3.5.4 Zero and span adjustment. See subsections 7.0.9.3 and 7.0.9.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to re-establish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero or span adjustment, verify linearity with a multipoint calibration (subsection 7.0.9.2) using at least 3 known pollutant concentrations, including zero.

7.3.6 Selection of Gas Dilution Flow Rates

The dilution flow rates used for the reference and candidate permeation devices should be selected carefully, in conjunction with selection of the analyzer range, to provide diluted concentrations for both the candidate and reference devices that fall preferably in the upper half, and in any case between 25 and 97 percent of the upper range limit of the measurement range of the analyzer. Potential assay error due to dilution flow rate measurement error will be greatly reduced if exactly the same dilution flow rates can be used for both the candidate and reference devices. This is feasible if the permeation rate of the candidate device is between 0.3 and 1.3 times the permeation rate of the reference device. Thus, if at all possible, select reference and candidate permeation devices having permeation rates that meet those limits, and then determine the pollutant and zero gas flow rates that will produce the highest analyzer responses within the analyzer's measurement range for both the reference and candidate devices.

If the same dilution flow rates cannot be used for both the candidate and reference devices, select different dilution flow rates for the candidate and reference devices to provide approximately equal diluted concentrations that fall in the upper half of the analyzer's measurement range.

7.3.7 Flow Meter Type and Flow Meter Calibration

The primary flow meter, as shown in Figure P1, measures in-line flow rates and does not operate at atmospheric pressure because of backpressure from downstream components. Also, this backpressure is variable, depending on the total flow rate. Thus, the type of flowmeter used must compensate for the variable in-line pressure. For this reason, a mass-type flow meter is recommended. Measurements from a pressure-sensitive flowmeter such as a rotameter or a volume meter must be carefully corrected for the actual meter pressure during the flow measurement. A non-venting pressure regulator may be inserted downstream of the flowmeter so that the flowmeter operates at a fixed pressure regardless of the total flow rate.

Alternatively, the flow rates can be measured at the outlet of the dilution apparatus, with the vent temporarily plugged. In this case, a volume-type meter such as a wet test meter or a bubble meter can be used, and flow measurements may be conveniently referenced to atmospheric pressure. Great care must then be exercised to insure that each measured flow rate remains constant between the time of measurement and the time of the assay.

The flow meter used should be stable, repeatable, linear, and have good resolu-

tion (readability). If possible, select flow rates or a flow meter range such that the measured flow rates fall in the upper half of the flow meter's range. The flow meter should be carefully calibrated at several flow rates to prove linearity. The calibration should be accurate to ±2 percent, referenced to an accurate flow or volume standard traceable to an NBS primary standard. The flow meter calibration should be checked and recertified periodically, as determined by stability information such as a chronological control chart of calibration stability. All volumetric flow rate measurements must be corrected or referenced to the same temperature and pressure conditions, such as EPA standard conditions (25 degrees C and 760 mm Hg) or the ambient temperature and pressure conditions prevailing in the laboratory during the assay.

Measurement of both dilution flow rates with the same flow meter tends to reduce systematic (proportional) flow measurement error if the flowmeter is linear (see Equation P1). Note particularly that flow measurement error is greatly reduced if exactly the same dilution flow rates can be used for both the reference and candidate devices.

7.3.8 Permeation Devices

7.3.8.1 Candidate permeation device. See subsections 7.0.8 and 7.3.2. Follow the manufacturer's instructions for equilibration and use of the candidate permeation device and for selecting the temperature at which it is to be assayed and certified. The candidate permeation device should be assayed at the same temperature at which it will be subsequently used, and if possible, in the same controlled-temperature chamber in which it will be used. The operating temperature of the device must be controlled to ±0.05 degree C and measured with an NBS-traceable thermometer accurate to ±0.1 degree C or better.

7.3.8.2 Reference permeation device. See subsections 7.0.2, 7.0.8.1, 7.0.8.2, and 7.3.2. Follow NBS's instructions for equilibration and use of the SRM permeation device standard and for selecting an operating temperature within its certified range. The operating temperature of the device must be controlled to ±0.05 degree C and measured with an NBS-traceable thermometer accurate to ±0.1 degree C or better.

7.3.8.3 Zero gas. See subsection 7.0.10. Use the same zero gas for dilution of both the candidate and reference devices.

7.3.9 Assay Procedure

1. Verify that the assay apparatus is properly configured as shown in Figure P1 and described in subsection 7.3.3.

2. Determine and establish the operating temperatures for the reference and candidate permeation devices in their respective temperature-controlled chambers. Install the permeation devices and, with zero gas flowing over both devices, allow ample time for the devices to equilibrate (see subsection 7.0.8.2).

3. Verify that the flow meter is properly calibrated (subsection 7.3.7).

4. Verify that the linearity of the analyzer has been checked within the last 3

months (see subsections 7.0.9.2, 7.0.9.5, and 7.3.4), that the zero and span are adjusted correctly (subsection 7.0.9.3), and that the analyzer is operating stably.

5. Determine and establish the dilution flow rates for the reference and candidate permeation devices that will be used for the assay (see subsections 7.3.6, 7.3.7, and 7.3.5.2). Ensure that the diluted candidate and reference device concentrations are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer. Also check that both the candidate and reference device dilution flow rates will provide enough flow for the analyzer, with sufficient excess to assure that no ambient air will be drawn into the vent, and without increasing the pressure of the sample delivered to the analyzer. If possible, use the same dilution flow rate for both candidate and reference devices. Also adjust the flow rate of the portion of the dilution flow that passes over the permeation devices (Valves V4, V5, and V6), and adjust the respective purge flow rates for each device (Valve V7) to approximately the same values.

6. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the diluted concentration from the reference device, and a measurement of the diluted concentration from the candidate device. Use valves V1, V2, and V3 to select each of the three concentrations for measurement. For each measurement, adjust the flow rates, if necessary, to those determined in step 5 and allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration (and any transformation of the response readings necessary for analyzer linearity). Do not translate or adjust the response readings via the calibration curve. Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.

7. Conduct at least 2 additional measurement triads similar to step 6 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure the reference concentration, then zero gas, then the candidate concentration for the second triad, and zero gas, candidate concentration, reference concentration for the third triad, etc.).

8. If any one or more of the measurements of the triad is invalid or abnormal for any reason, discard all three measurements of the triad and repeat the triad.

9. For each triad of measurements, calculate the assay permeation rate of the candidate permeation device as follows:

$$P_C = P_r \frac{Q_C}{Q_r} \frac{R_C - R_Z}{R_r - R_Z} \qquad \text{Equation P1}$$

where: P_C = Assay permeation rate of the candidate permeation device, $\mu g/min$;
P_r = Permeation rate of the reference permeation standard, $\mu g/min$;
Q_C = Flow rate of the dilution flow for the candidate permeation device, cm^3/min;*

7.4 PROCEDURE P2: ASSAY AND CERTIFICATION OF A PERMEATION DEVICE REFERENCED TO A COMPRESSED GAS STANDARD

7.4.1 Applicability

This procedure may be used to assay the permeation rate of a candidate SO_2 and NO_2 permeation device pollutant standard, based on the concentration of a compressed gas (cylinder) reference standard of the same pollutant compound, and certify that the assayed permeation rate thus established for the candidate standard is traceable to the reference standard. The procedure employs a low-concentration range (ambient level) pollutant gas analyzer to compare quantitatively diluted concentrations from the permeation device with quantitatively diluted concentrations from the reference standard for the assay of the candidate permeation device.

7.4.2 Limitations

1. The analyzer's response (or transformed response) must be linear with respect to concentration.

2. A quantitatively accurate dilution and flow measurement system is required. The accuracy of the assay is fully dependent on the accuracy of the reference gas flow measurement.

3. A source of clean, dry zero gas is required.

4. This procedure is designed to assay the absolute permeation rate of a candidate permeation device, using a specially designed external assay dilution system; the procedure does not accommodate the certification of a candidate permeation device standard together with its own self-contained dilution/flow measurement system.

7.4.3 Assay Apparatus

Figure P2 illustrates the components and configuration of the assay apparatus, including a common dilution system for both the reference gas and the candidate permeation device. The configuration is designed to allow convenient routing of zero gas and diluted concentrations of the reference gas and the candidate permeation device, in turn, to the analyzer for measurement, as selected by valves V1, V2, and V3. One flow controller controls the dilution flow rate for both the reference gas and the candidate permeation device, and these flow rates are measured by a single, common (zero gas) flow meter. The flow controller may be a needle valve, pressure regulator, electronic flow controller, or other means of flow control. Flow rates should be controlled to within 1 percent variation during the assay.

When the diluted concentration from the candidate permeation device is selected for measurement by valves V1 and V2, a portion (usually 10 to 500 cm^3/min) of the total dilution flow passes through the temperature-controlled permeation device container to sweep up the permeated pollutant gas. This sweep flow rate is adjusted by valve V5 and monitored by an auxiliary flow meter. This auxiliary flow meter need not be accurately calibrated, since only the total flow, measured by the zero gas flow meter, is used in the dilution calculation. When the diluted reference gas

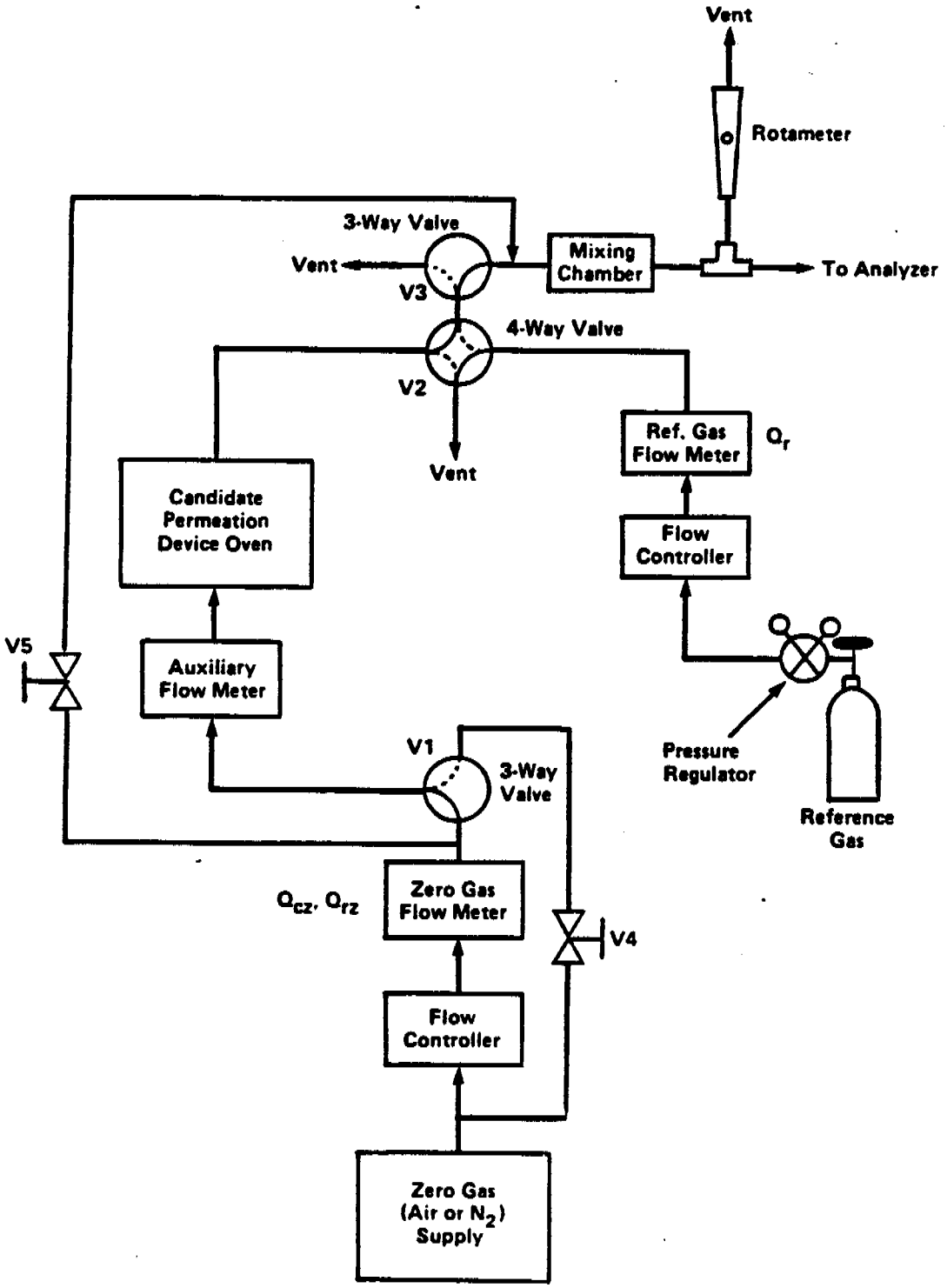


Figure P2. Suggested assay apparatus for Procedure P2.

concentration is selected for measurement by valves V1 and V2, the candidate permeation device receives an approximately equivalent zero gas purge flow rate, controlled by valve V4, to avoid a high pollutant concentration accumulation. This purge flow is vented by valve V2 and is not measured by the zero gas flow meter. The reference gas flow rate is controlled by a second flow controller and measured by a second, accurately calibrated flow meter. Both the dilution and reference gas flows should be controlled to within 1 percent variation during the assay.

If it is necessary to use different zero gas dilution flow rates for the reference gas and the candidate permeation device (see subsection 7.4.6), separate flow controllers for the two flow rates may be used, if desired; however, the same flow meter should be used to measure both flow rates to help reduce systematic (proportional) flow measurement errors.

The mixing chamber combines the gas flows and should be designed to provide turbulence in the flow to insure thorough mixing of the two gas streams. The diluted pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess flow and insures that the assay concentrations sampled by the analyzer are at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. See also subsection 7.0.4. Check the apparatus carefully for leaks and correct all leaks before use.

7.4.4 Analyzer

See subsection 7.0.9.1. The pollutant gas analyzer must have a linear response function and a calibrated range capable of measuring the diluted concentrations of both the candidate permeation device and the reference gas. It must have good resolution (readability), good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in the reference gas. A suitable analyzer may be selected from the list of EPA-designated reference and equivalent method analyzers[8]. If the balance gas of the reference standard must be different from the zero gas used for dilution (air versus nitrogen or different proportions of oxygen, for example), either a high dilution ratio (> 50:1) should be used, or the analyzer must be proven to be insensitive to the two gases. The latter may be accomplished by showing no difference in analyzer response when measuring pollutant concentrations diluted with identical flow rates of the two gases.

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

7.4.5. Analyzer Calibration

7.4.5.1 Multipoint calibration. See subsections 7.0.9.2 and 7.0.9.4.

7.4.5.2 Calibration range. The calibrated range of the analyzer must include the diluted concentrations of both the candidate permeation device and the reference gas (see subsection 7.4.6). The higher concentration should not exceed 97 percent of the upper range limit, and the lower concentration should not be less than 25 percent of the upper range limit (assuming a lower range limit of

zero). Since the selection of the dilution flow rates used provides great flexibility in the choice of concentrations to be measured by the analyzer, the analyzer range should be selected based on optimum accuracy, stability, and linearity.

7.4.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 7.0.9.5). Many low-range analyzers of the type that may be used for this procedure are sufficiently linear. If not, they usually have a predictable non-linear response characteristic that can be mathematically transformed to produce a linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve because physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

7.4.5.4 Zero and span adjustment. See subsections 7.0.9.3 and 7.0.9.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to re-establish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero and span adjustment, verify linearity with a multipoint calibration (subsection 7.0.9.2) using at least three known pollutant concentrations, including zero.

7.4.6 Selection of Gas Dilution Flow Rates

The dilution flow rates used for the reference gas and the candidate permeation device should be selected carefully, in conjunction with selection of the analyzer range, to provide diluted concentrations for both the reference gas and the candidate permeation device that fall preferably in the upper half, and in any case between 25 and 97 percent of the upper range limit of the measurement range of the analyzer. Potential assay error due to dilution flow rate measurement error will be reduced if exactly the same dilution flow rates can be used for both the reference gas and the candidate permeation device. This should be feasible by appropriate selection of the reference gas flow rate. Select a combination of reference gas flow rate and zero gas dilution flow rate that produces approximately equal diluted reference gas and candidate device concentrations that fall in the upper half of the analyzer's measurement range.

7.4.7 Flow Meter Type and Flow Meter Calibration

The zero gas and reference gas flow meters, as shown in Figure P2, measure in-line flow rates and do not operate at atmospheric pressure because of backpressure from downstream components. Also, this backpressure is variable, depending on the total flow rate. Thus, the flowmeters must be of non-contaminating design and must compensate for the variable in-line pressure. For this reason, mass-type flow meters are recommended. Measurements from pressure-sensitive flowmeters such as rotameters or volume meters must be carefully corrected for the actual meter pressure during the flow measurement. A non-venting pressure regulator may be inserted

downstream of the flowmeter so that the flowmeter operates at a fixed pressure regardless of the total flow rate.

Alternatively, the flow rates can be measured at the outlet of the dilution apparatus, with the vent temporarily plugged. In this case, a volume-type meter such as a wet test meter or a bubble meter can be used, and flow measurements may be conveniently referenced to atmospheric pressure. However, each flow rate must be measured independently, in turn, while the other flow rate is set to zero. Accordingly, great care must be exercised to insure that each measured flow rate remains constant when combined with the other flow rate and between the time of measurement and the time of the assay.

The flow meters used should be stable, repeatable, linear, and have good resolution (readability). If possible, select flow rates or flow meter ranges such that the measured flow rates fall in the upper half of the flow meters' ranges. It is important to measure both dilution flow rates with the same flow meter. This tends to reduce systematic (proportional) flow measurement error for the zero gas flow measurements if the flowmeter is linear, and particularly if the same flow rates are used for both the reference gas and the candidate permeation device. The flow meters should be carefully calibrated at several flow rates to prove linearity. The calibration of the zero gas flow meter should be accurate to ±2 percent, referenced to an accurate flow or volume standard traceable to an NBS primary standard. This flow meter calibration should be checked and recertified periodically, as determined by stability information such as a chronological control chart of calibration stability.

The accuracy of the assay is critically dependent on the absolute accuracy of the reference gas flow rate measurement. Accordingly, the calibration of the reference gas flow meter must be accurate to ±1 percent, referenced to an NBS-traceable flow or volume standard. The calibration of this flowmeter should be verified immediately prior to the assay. All flow measurements must be corrected to EPA-standard conditions of 25 degrees Celsius and 760 mm Hg pressure to be consistent with equation P2.

7.4.8 Candidate Permeation Device

See subsections 7.0.8 and 7 .4.2. Follow the manufacturer's instructions for equilibration and use of the permeation device and for selecting the temperature at which it is to be assayed and certified. The candidate permeation device should be assayed at the same temperature at which it will be subsequently used and, if possible, in the same temperature-controlled chamber in which it will be used. The operating temperature of the device must be controlled to ±0.05 degree C and measured with an NBS-traceable thermometer accurate to ±0.1 degree C or better.

7.4.9 Reference Gas Standard

See subsections 7.0.2, 7.0.7.4, and 7.4.6.

7.4.10 Zero Gas

See subsection 7.0.10. If possible, the zero gas should be the same as the balance gas of the reference standard.

7.4.11 Assay Procedure

1. Verify that the assay apparatus is properly configured as shown in Figure P2 and described in subsection 7.4.3.

2. Determine and establish the operating temperature for the candidate permeation device in its temperature-controlled chamber. Install the candidate permeation device and--with a suitable purge flow--allow ample time for the device to equilibrate (see subsection 7.0.8.2).

3. Verify that the flow meters are properly calibrated, particularly the reference gas flow meter (see subsection 7.4.7).

4. Verify that the linearity of the analyzer has been checked within the last 3 months (see subsection 7.0.9.2, 7.0.9.5, and 7.4.4), that the zero and span are adjusted correctly (subsection 7.0.9.3), and that the analyzer is operating stably.

5. Determine and establish the dilution flow rates for the reference gas and the candidate permeation device that will be used for the assay (see subsections 7.4.6 and 7.4.5.2). Ensure that the diluted reference gas and candidate permeation device concentrations are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer. Also check that both the reference gas and candidate device dilution flow rates will provide enough flow for the analyzer, with sufficient excess to assure that no ambient air will be drawn into the vent, and without increasing the pressure of the sample delivered to the analyzer. If possible, use the same dilution flow rate for both the reference gas and the candidate permeation device. Also adjust the flow rate of the portion of the dilution flow that passes over the permeation device (valve V5), and adjust the purge flow rate (valve V4) to approximately the same value.

6. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the diluted reference gas concentration, and a measurement of the diluted concentration from the candidate permeation device. Use valves V1, V2, and V3 to select each of the three concentrations for measurement. For each measurement, adjust the flow rates, if necessary, to those determined in step 5 and allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration (and any transformation of the response readings necessary for analyzer linearity). Do not translate or adjust the response readings via the calibration curve. Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.

7. Conduct at least 2 additional measurement triads, similar to step 6 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure the reference gas concentration, then zero gas, then the candidate permeation device concentration for the second triad, and zero gas, candidate concentration, reference concentration for the third triad, etc.).

8. If any one or more of the measurements of a triad is invalid or abnormal for

any reason, discard all three measurements of the triad and repeat the triad.

9. For each triad of measurements, calculate the assay permeation rate of the candidate permeation device as follows:

$$P_C = C_r M \frac{Q_r}{Q_r + Q_{rz}} \frac{Q_{cz}}{24,470} \frac{R_c - R_r}{R_r - R_z} \qquad \text{Equation P2}$$

where: P_C = Assay permeation rate of the candidate permeation device under certification, μg/min;
C_r = Concentration of the undiluted reference gas standard, ppm;
M = Molecular weight of the pollutant compound (64.07 for SO_2 or 46.0 for NO_2), g/mole;
Q_r = Flow rate of the (undiluted) reference gas, std cm^3/min*;
Q_{CZ} = Flow rate of the zero gas dilution flow for the candidate permeation device, std cm^3/min*;
Q_{rz} = Flow rate of the zero gas dilution flow for the reference gas, std cm^3/min*;
24,470 = Molar volume of gas at 25 degrees C and 760 mm Hg, std cm^3/mole*;
R_c = Stable response reading of the analyzer to the diluted concentration from the candidate permeation device; analyzer response units**;
R_z = Stable response reading of the analyzer to the zero gas, analyzer response units**;
R_r = Stable response reading of the analyzer to the diluted concentration of the reference gas, analyzer response units**.

*All flow measurements must be corrected to EPA-standard conditions of 25 degrees C and 760 mm Hg.

**Analyzer response units are the units used to express the direct response readings of the analyzer, such as volts, millivolts, percent of scale, etc. DO NOT convert these direct response readings to concentration units with the calibration curve or otherwise adjust these readings except for transformation necessary to achieve response linearity.

Note that when the same dilution flow rate is used for both the candidate permeation device and the reference gas ($Q_{CZ} = Q_{rz}$) and the reference gas dilution flow rate is much higher than the reference gas flow rate ($Q_{rz} \gg Q_r$), then ($Q_r + Q_{rz}$) is approximately equal to Q_{CZ}, and systematic (proportional) error in the zero flow rate measurement is reduced. However, no similar reduction of systematic error for the reference gas flow rate (Q_r) is available.

10. Calculate the mean of the 3 (or more) valid assays. Calculate the percent difference of each assay from the mean. If any one of the assay values differs from the mean by more than 1.5%, discard that assay value and conduct another triad of measurements to obtain another assay value. When at least 3 assay values all agree within 1.5% of their mean, report the mean value as the certi-

fied permeation rate of the candidate permeation device. For new permeation devices, a reassay after at least 24 hours is required to check the stability of the device; see subsection 7.0.8.4.

11. Compare the assay permeation rate with the permeation rate determined at the previous assay/certification. If these permeation rates do not agree within 4 percent, repeat the assay after allowing additional time for equilibration of the permeation device.

7.4.12 Stability test for new permeation devices

See subsection 7.0.8.3 and 7.0.8.4.

7.4.13 Certification Documentation

See subsections 7.0.5 and 7.0.6.

7.2.14 Recertification Requirements

See subsection 7.0.8.3.

7.5 References.

1. Code of Federal Regulations, Title 40, Part 50, "National Ambient Air Quality Measurement Methodology".

2. Code of Federal Regulations, Title 40, Part 58, "Ambient Air Quality Surveillance," Appendixes A and B.

3. Code of Federal Regulations, Title 40, Part 60, "Standards of Performance for New Stationary Sources," Appendix A, Method 20 (1982).

4. Standards of Performance for New Stationary Sources; Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination, promulgated in the Federal Register, June 4, 1987, pp. 21003-21010.

5. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. EPA-600/7-81-010. Joint publication by NBS and EPA, May 1981. Available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory (MD-77), Research Triangle Park, NC 27711.

6. Shores, R. C. and F. Smith, "Stability Evaluation of Sulfur Dioxide, Nitric Oxide, and Carbon Monoxide Gases in Cylinders. NTIS No. PB 85-122646. Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

7. Method 6A and 6B, "Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide Emissions from Fossil Fuel Combustion Sources," Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Section 3.13.8, July 1986. Available from the U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH 45268.

8. "List of Designated Reference and Equivalent Methods." Current edition available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, NC 27711.

United States
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Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

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Air

EPA

Control of Volatile Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems

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CTG

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements in Agency documents in metric units. Dual units are sometimes given in the text for clarity. Listed below are abbreviations and conversion factors for English equivalents of metric units. Frequently used measurements are also presented in dual units below for the reader's convenience.

METRIC UNIT	ALTERNATE UNIT	CONVERSION
centimeter (cm)	inches	cm x 0.394 = in
Pascals (Pa)	atmospheres	Pa x 9.87×10^{-6} = atm
	inches of water	Pa x 4.02×10^{-3} = inches of water
liters (l)	gallons	l x 0.264 = gal

FREQUENTLY USED MEASUREMENTS

750 pascals ∿ 3 inches of water

1500 pascals ∿ 6 inches of water

4500 pascals ∿ 18 inches of water

6250 pascals ∿ 25 inches of water

2.5 cm ∿ 1 inch

.625 cm ∿ 1/4 inch

20,000 liters ∿ 5280 gallons

I. BACKGROUND

This guideline is related to the control of volatile organic compounds (VOC) from gasoline tank trucks and vapor collection systems at bulk terminals, bulk plants and service stations. Guideline documents have already been published on bulk plants,[1] bulk terminals[2] and service stations.[3] The intent of this guideline is to define leak tight conditions and related test procedures for vapor collection systems and tank trucks while loading and unloading at these facilities. VOC emitted from leaks in collection equipment are primarily C_4 and C_5 paraffins and olefins which are photochemically reactive (precursors to oxidants).

Methodology described in this guideline represents the presumptive norm or reasonably available control technology (RACT) that can be applied to an existing facility. RACT is defined as the lowest emission limit that a particular source is capable of meeting by the application of control technology that is reasonably available considering technological and economic feasibility. It may require technology that has been applied to similar, but not necessarily identical, source categories. It is not intended that extensive research and development be conducted before a given control technology can be applied to the source. This does not, however, preclude requiring a short-term evaluation program to permit the application of a given technology to a particular source. This latter effort is an appropriate technology-forcing aspect of RACT.

A. NEED TO REGULATE

Control techniques guidelines are being prepared for source categories that emit significant quantities of air pollutants in areas of the country

where National Ambient Air Quality Standards (NAAQS) are not being attained. Vapor balance and processor systems have been applied to bulk plants, terminals, and service stations in many areas of the nation. Leaks from tank trucks and vapor collection systems should be minimized to ensure that vapor control systems at these systems function effectively.

B. CONTROL APPROACH

The approach described in this document is to ensure that good maintenance practices are followed. Maintenance would be enforced through the surveillance and periodic testing of suspect leak points. It should be noted that while some leak sources (such as vapor piping joints) may stay in leak tight condition for extended periods of time, others (such as pressure and vacuum vents, and hatch seals) may leak shortly after maintenance. It is expected that compliance with the suggested control measure will in some cases require replacement of truck pressure and vacuum vents and dome covers. In addition, a greater degree of surveillance and maintenance will be needed at bulk plants and terminals equipped with top loading (vapor head) systems than at those using bottom loading. Additional information on control techniques, costs, and monitoring procedures is presented in an EPA report.[4]

II. REGULATORY APPROACH

A. AFFECTED FACILITIES

The two separate affected facilities are gasoline tank trucks that are equipped for vapor collection and the vapor collection systems at bulk terminals, bulk plants, and service stations that are equipped with vapor balance and/or vapor processing systems.

B. RECOMMENDED REGULATION

B.1 Gasoline Tank Trucks

Gasoline truck tanks and their vapor collection systems shall not sustain a pressure change of more than 750 pascals (3 inches of H_2O) in 5 minutes when pressurized to 4500 pascals (18 inches of water) or evacuated to 1500 pascals (6 inches of water) using the test procedure described in Appendix A. In addition, there are to be no avoidable visible liquid leaks. Invariably there will be a few drops of liquid from disconnection of dry breaks in liquid lines even when well maintained; these few drops should be allowed.

B.2 Vapor Collection Systems

B.2.1 - During loading or unloading operations at service stations, bulk plants and bulk terminals, there shall be no reading greater than or equal to 100 percent of the lower explosive limit (LEL, measured as propane) at 2.5 centimeters around the perimeter of a potential leak source as detected by a combustible gas detector using the test procedure described in Appendix B. In addition, there are to be no avoidable visible liquid leaks. Invariably there will be a few liquid drops from the disconnection of well maintained bottom loading dry breaks and the raising of well maintained top loading vapor heads; these few drops should be allowed. The vapor collection system includes all piping, seals, hoses, connections, pressure-vacuum vents, and other possible leak sources between the truck and the vapor processing unit and/or the storage tanks and vapor holder; and

B.2.2 - The vapor collection and vapor processing equipment must be designed and operated to prevent gauge pressure in the tank truck from exceeding 4500 pascals (18 inches of water) and prevent vacuum from exceeding 1500 pascals (6 inches of water).

C. MONITORING REQUIREMENTS

C.1 Gasoline Tank Trucks

Gasoline truck tanks must be certified leak tight as described in Section B.1 annually.

In addition, truck tanks can be monitored by regulatory agencies as needed during loading and unloading using the combustible gas detection procedure described in B.2.1, provided that the requirements in Section B.2.2 are met. Trucks with leaks greater than or equal to 100 percent of the LEL are to be repaired within 15 days and be required to take and pass the pressure and vacuum test described in Section B.1 The truck tank and its vapor collection system includes all piping, seals, hoses, connections, hatch covers, pressure vacuum vents, vapor hoods and other possible leak sources on the truck tank.

C.2 Vapor Collection Systems

Vapor collection systems can be monitored by regulatory agencies as needed using the combustible gas detection procedure described in B.2.1.

D. RECORD KEEPING AND REPORTING REQUIREMENTS

D.1 Gasoline Tank Trucks

Each truck must have a sticker displayed on each tank indicating the identification number of the tank and the date each tank last passed the pressure and vacuum test described in Section B.1. This sticker must be located near the Department of Transportation Certification plate (DOT, Title 49, Part 178.340-10b).

D.2 Vapor Collection System

Bulk terminal, bulk plant and service station owners or operators must keep records for two years indicating the last time the vapor collection facility

passed the requirements described in B.2 and identifying points at which VOC leakage exceeded the provisions of Section B.2.1.

E. OTHER CONSIDERATIONS

Presently, there is limited information available on the amount of monitoring necessary to ensure that leaks are kept to the limits described above. Therefore, regulations should allow for modifications in the monitoring schedule when experience proves it to be either inadequate or excessive. If, after over one year of monitoring, i.e., at least two complete annual checks, the operator of an affected facility feels that modifications of the requirements are in order, he may request in writing to the air pollution control officer that a revision be made. The submittal should include data that have been developed to justify any modifications in the monitoring schedule. On the other hand, if the air pollution control officer finds an excessive number of leaks during an inspection, or if the operator finds an excessive number of leaks during scheduled monitoring, consideration should be given to increasing the frequency of inspections.

III. COMPLIANCE TEST METHOD AND MONITORING TECHNIQUES

The measurement procedures that were developed for determining leak tightness of truck tanks and vapor control systems at bulk terminals, bulk plants, and service stations, are discussed in this section. The presentation covers the various methods considered with the advantages and disadvantages of each, testing problems encountered, and the accuracy, reliability, and allowable modifications of the recommended methods.

A. COMPLIANCE TEST METHOD DESCRIPTION

A.1 General Description and Background

The recommended compliance test method as detailed in Appendix A can be used to determine the leak-tightness of gasoline truck tanks. Pressure and vacuum are applied to the tanks of a gasoline delivery truck and the change in pressure/vacuum is recorded after a specified period of time. The recommended regulation in Section II.B.1 in effect defines a "leak tight condition" which is equivalent to 99 percent recovery efficiency during vapor transfer from a truck tank. The recommended compliance procedure is actually an equipment performance criteria rather than a true emission measurement test. However, emissions from a truck tank can be estimated from the known required degree of leak-tightness.

Developmental work on a leak test method was performed by the California Air Resources Board (CARB), San Diego Air Pollution Control District (SDAPCD), and Standard Oil of California, among others. Leak-tightness regulations have been in effect in California for over two years. The pressure and vacuum limits recommended in Section II.B.1 are based on a consensus of the above mentioned groups, and on an EPA field testing program which was conducted in order to evaluate the leak test method and performance criteria. The study shows that EPA's recommended performance criteria is realistic and achievable and the test method is inexpensive, reliable, and repeatable.[5]

A.2 Modifications

There are two areas of common modifications to the test procedure in Appendix A.

The recommended EPA compliance test procedure uses air to pressurize and evacuate the truck tank. In EPA field testing, this was

found to be the most convenient and inexpensive procedure. However, some owners prefer loading and draining the tank with a liquid, usually diesel fuel or water, to create the required pressure and vacuum. This is an acceptable and equivalent alternative.

The EPA procedure also requires that gasoline vapors be purged from the truck tank before conducting the leak-tightness test. This is easily accomplished by carrying a diesel load immediately prior to the compliance test or blowing air into the tank with the dome lids open. Gasoline vapors in the tank cause testing inconsistencies. With volatile vapors, the tank pressure varies more readily with slight changes in temperature. However it is possible to test without purging the gasoline vapors if there is enough time for the vapors to stabilize and reach a constant temperature in the covered testing area. One can ensure that the vapors have stabilized and are not affecting the test results by conducting the test two times with the same results.

A.3 Effectiveness

The EPA field testing program[6] and a recent CARB study[7] both indicate that truck tanks rarely remain in a leak-tight condition within two or three months after the compliance test. After the initial leak-tightness compliance test, the leaks that occur are usually easily detectable and correctable with good normal maintenance. It is hoped that conducting unannounced spot-checks with monitoring procedures described in the following section, will encourage more frequent and effective maintenance.

B. DESCRIPTION OF MONITORING TECHNIQUES

B.1 Background

Monitoring techniques for leak detection were developed to ensure the continuing existence of leak-tight conditions between compliance tests. A test method was sought that would give pass/fail compliance information for leakage from truck tanks and vapor control systems at bulk terminals, bulk plants, and service stations. It was desired that the monitoring test method be low cost, quick, and used without disturbing normal operations. It is essential that leak detection by a monitoring technique be be equivalent to the leak-tightness criteria of the pressure/vacuum compliance test.

Several leak detection monitoring methods were investigated in EPA's field testing program: combustible gas detector, sonic detector, bubble indication, sensory detection (i.e., sound, sight, smell, touch), vapor to liquid volume ratio, quick leak decay, and bag capture. Bag capture and combustible gas detector were both found to be reliable, quick, low cost, and closely equivalent to the compliance criteria. The recommended method is the combustible gas detector procedure because it is more reliable and can be applied to top and bottom-loaded tanks. However, the bag capture procedure is an acceptable alternative for leak detection of bottom-loaded tanks. A discussion of the other non-recommended methods is included in an EPA contractor report.[8]

B.2 Description of Combustible Gas Detector Procedure

B.2.1 - Selection and applicability. The combustible gas detector is the recommended leak detection method because it is simple, quick, inexpensive, reliable, and non-subjective. It can be used for leak

detection of truck tanks and vapor control systems without disturbing normal operations. Although a combustible gas detector is often considered a qualitative monitoring instrument, the detailed specifications of its use and operation, as defined in Appendix B, make this an acceptable procedure.

Leak detection of truck tanks by combustible gas detector correlates well with the pressure/vacuum compliance criteria in Section II.B.1, when a leak is defined as a meter reading greater than or equal to 100 percent LEL as propane. The monitoring procedure will correctly identify 42 percent of the non-complying tanks, while incorrectly identifying only 5 percent of the complying tanks.[9] The combustible gas detector procedure is purposely designed to detect gross violations of the leak-tightness performance criteria, but will not confirm compliance, i.e. tanks with marginal violations will evade detection.

B.2.2 - Equipment and operation specifications. In order to make leak detection by combustible gas detector more reliable and repeatable, equipment and operation specifications are tightly defined. For valid monitoring, it is important that the procedure is the same as the one used in EPA's field testing and data collection.

Equipment specifications require that the meter is calibrated to propane, inside probe diameter is 0.625 cm (1/4 inch), and response time for full-scale deflection with the sampling probe and line attached is less

than 8 seconds. A standard calibration gas is needed to standardize the detector response. The selection of propane as the calibration gas is arbitrary. Propane was used for calibration in the data gathering tests, and it is probably the most readily available gas.

The probe diameter requirement allows some dilution air drawn in if the leak is very small, and thus the detector will not register a leak. If the same leak were sampled with a smaller diameter probe, the sample line would be filled with leaked vapors with no dilution, and a leak would be detected. Thus, a larger probe diameter ensures that only insignificant leaks are registered.

The response time requirement ensures that the meter pump is strong enough to draw the sample quickly through the sampling probe and line. This quick response is necessary since there is little time during a loading to check all potential sources of leakage.

Operation of the combustible gas detector for leak monitoring is also tightly defined to eliminate variability. However, any arbitrariness or sloppiness in the procedure is in favor of the truck tank owner. Operation specifications require measurement at 2.5cm (1 inch) distance from the leak source, positioning the probe in the path of (parallel to) the vapor flow, moving the probe slowly locating the point of highest meter response, and blocking wind interference when possible. Measurement at 2.5cm distance allows some dilution if only a very small leak exists. The distance can be maintained during monitoring by putting a 2.5cm extension on the probe tip. Maintaining this distance is essential or else insignificant leaks will be detected.

Higher meter readings will be obtained when the probe is properly positioned, moved slowly, and if care is taken to locate the center of a leak. These specifications were followed diligently in the testing which was used to develop the data base and correlation with the compliance test.

Any sloppiness in these areas would detect less leaks and be in favor of the truck. Furthermore, the field testing was conducted on windless, hot days. Winds would dilute the vapors before detection, and cooler temperatures would reduce the hydrocarbon concentration. Again, under these conditions, the meter would detect less leakage, and the variability in the method favors the truck tank owners.

B.2.3 - Modifications. It should be noted that the adequacy of the combustible gas detector method, and the LEL level where the method is usable, are based on the performance test criteria in Section II.B.1. If other criteria are used to define a leak-tight tank, the detector method will have to be re-evaluated to determine the applicable LEL level to be used for monitoring.

The combustible gas detector method can be made less stringent by simply increasing the sampling distance. However, this is not recommended since the purpose of monitoring is to ensure compliance, and the recommended procedure is closely equivalent to the leak-tightness performance test.

B.3 Description of Bag Capture Procedure

B.3.1 - Background. The bag capture procedure is an acceptable alternative method for leak monitoring of bottom-loaded truck tanks. The complete procedure is included in Appendix C. The procedure was developed by San Diego Air Pollution Control District, and has been in use for over two years. The volume of leakage is measured directly by placing calibrated bags over all dome covers. The volume of allowable leakage is calculated from the parameters of the pressure/vacuum compliance test (as shown in equation 7.1, Appendix C).

This procedure, like the combustible gas detector, is designed to detect gross violations while not detecting marginal violations. Again, any sloppiness or variability in the method is in the favor of the truck tank. Only leakage from dome covers, hatches, and relief valves is captured; leakage from the tank vapor collection system is not included. If the seal between the bag apparatus and tank is not tight enough, the leakage may be underestimated. Furthermore, the allowable volume of leakage is based on 4500 pascals (18 inches H_2O) pressure, which rarely occurs during loadings.

B.3.2 - Disadvantage and Advantages. This method does have serious drawbacks. It can only be applied to bottom-loaded tanks. Some tanks cannot be monitored because the equipment configuration prevents a tight seal. Also, not all potential leakage sources are monitored.

On the other hand, the method has some real advantages. The equipment is very inexpensive and easy to use. It can be applied regardless of the type of vapors inside. Emissions can be measured directly, instead of by estimation. In San Diego, with this method, a leak has never been incorrectly detected for a complying tank. Finally, the bag method can be modified to detect leaks for any degree of leak-tightness if the parameters of the performance test are altered.

Many agencies and companies resist the use of a combustible gas detector. The bag capture method is a good alternative. It is probably less stringent than the explosimeter, but it will still detect all gross violations.

C. VAPOR CONTROL SYSTEM MONITORING

C.1 Pressure and Vacuum Limits.

The regulation in Section II.B.2.2 requires that the pressure/vacuum in a vapor control system remain within the pressure/vacuum limits of the truck tank compliance test. This ensures that a vapor control system will not create a leak on a tank. During leak detection monitoring of the tanks, the pressure must remain within these limits or else the detection of any leak will be invalidated.

C.2 Leak Detection.

The combustible gas detector procedure in Appendix B can be applied to potential sources of leakage at terminal, plant, and service station vapor control systems. These points of leakage can be easily identified and corrected during normal maintenance, and once corrected remain in leak tight condition for extended periods of time.

This application of the combustible gas detector procedure is a qualitative measurement; there is no way to relate this leak detection to emission levels.

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8. Reference 4, Op. Cit.

9. Reference 4, Op. Cit.

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Control of Volatile Organic Compound Leaks from Gasoline Tank Trucks and Vapor Collection Systems

Emission Standards and Engineering Division
Chemical and Petroleum Branch

W. VA. AIR POLLUTION CONTROL COMM.

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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APPENDIX A

PRESSURE-VACUUM TEST PROCEDURES
FOR LEAK TIGHTNESS OF TRUCK TANKS

1. PRINCIPLE

Pressure and vacuum are applied to the compartments of gasoline truck tanks and the change in pressure/vacuum is recorded after a specified period of time.

2. APPLICABILITY

This method is applicable to determining the leak tightness of gasoline truck tanks in use and equipped with vapor collection equipment.

3. DEFINITIONS

3.1 Truck tank. Any container, including associated pipes and fittings, that is used for the transport of gasoline.

3.2 Compartment. A liquid-tight division of a truck tank.

3.3 Truck tank vapor collection equipment. Any piping, hoses, and devices on the truck tank used to collect and route the gasoline vapors in the tank to the bulk terminal, bulk plant, or service station vapor control system.

4. APPARATUS

4.1 Pressure source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the truck tank to 6250 pascals (25 inches H_2O) above atmospheric pressure.

4.2 Regulator. Low pressure regulator for controlling pressurization of the truck tank.

4.3 Vacuum source. Vacuum pump capable of evacuating the truck tank to 2500 pascals (10 inches H_2O) below atmospheric pressure.

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4.4 Manometer. Liquid manometer, or equivalent, capable of measuring up to 6250 pascals (25 inches H_2O) gauge pressure with $\pm$ 25 pascals ($\pm$ 0.1 inch H_2O) precision.

4.5 Test cap for vapor recovery hose fittings. This cap should have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure/vacuum supply hose.

4.6 Pressure/vacuum relief valves. The test apparatus shall be equipped with an in-line pressure/vacuum relief valve set to activate at 7000 pascals (28 inches H_2O) above atmospheric pressure or 3000 pascals (12 inches H_2O) below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

4.7 Caps for liquid delivery line.

4.8 Pressure/vacuum supply hose.

5. PRETEST CONDITION

5.1 Purging of vapor. The truck tank shall be purged of gasoline vapors and tested empty. The tank may be purged by any safe method such as flushing with diesel fuel or heating fuel.

5.2 Location. The truck tank shall be tested where it will be protected from direct sunlight.

6. TEST PROCEDURE

6.1 The dome covers are to be opened and closed.

6.2 Connect static electrical ground connections to tank. Attach the delivery and vapor hoses, remove the delivery elbows, and plug the liquid delivery fittings.

6.3 Attach the test cap to the vapor recovery line of the truck tank.

6.4 Connect compartments of the tank internally to each other if possible. (If not possible, each compartment must be tested separately.)

6.5 Connect the pressure/vacuum supply hose and the pressure/vacuum relief valve to the shut-off valve. Attach the pressure source to the hose. Attach a manometer to the pressure tap.

6.6 Open the shut-off valve in the vapor recovery hose cap. Applying air pressure slowly, pressurize the tank, or alternatively the first compartment, to 4500 pascals (18 inches H_2O).

6.7 Close the shut-off valve and allow the pressure in the truck tank to stabilize, adjusting the pressure if necessary to maintain 4500 pascals (18 inches H_2O). When the pressure stabilizes, record the time and initial pressure.

6.8 At the end of 5 minutes, record the time and final pressure.

6.9 Disconnect the pressure source from the pressure/vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

6.10 Connect the vacuum source to the pressure/vacuum supply hose.

6.11 Slowly evacuate the tank, or alternatively the first compartment, to 1500 pascals (6 inches H_2O).

6.12 Close the shut-off valve and allow the pressure in the truck tank to stabilize, adjusting the pressure if necessary to maintain 1500 pascals (6 inches H_2O) vacuum. When the pressure stabilizes, record the time and initial pressure.

6.13 At the end of 5 minutes, record the time and final pressure.

6.14 Repeat steps 6.5 through 6.13 for each compartment if they were not interconnected.

7. ALTERNATIVE TEST METHODS

Techniques, other than specified above, may be used for purging and pressurizing the truck tanks, if prior approval is obtained from the air pollution control officer. Such approval will be based upon demonstrated equivalency with the above method.

APPENDIX B

GASOLINE VAPOR LEAK DETECTION PROCEDURE
BY COMBUSTIBLE GAS DETECTOR

1. PRINCIPLE

A combustible gas detector is used to indicate any incidence of leakage from gasoline truck tanks and vapor control systems. This qualitative monitoring procedure is an enforcement tool to confirm the continuing existence of leak-tight conditions.

2. APPLICABILITY

This method is applicable to determining the leak-tightness of gasoline truck tanks during loading without taking the truck tank out of service. The method is applicable only if the vapor control system does not create back-pressure in excess of the pressure limits of the truck tank compliance leak test. For vapor control systems, this method is applicable to determining leak-tightness at any time.

3. DEFINITIONS

3.1 Truck tank. Any container, including associated pipes and fittings, that is used for the transport of gasoline.

3.2 Truck tank vapor collection equipment. Any piping, hoses, and devices on the truck tank used to collect and route the gasoline vapors in the tank to the bulk terminal, bulk plant, or service station vapor control system.

3.3 Vapor control system. Any piping, hoses, equipment, and devices at the bulk terminal, bulk plant, or service station, which is used to collect, store, and/or process gasoline vapors.

4. APPARATUS AND SPECIFICATIONS

4.1 Manometer. Liquid manometer, or equivalent, capable of measuring up to 6250 pascals (25 inches H_2O) gauge pressure with $\pm$25 pascals (0.1 inch H_2O) precision.

4.2 Combustible gas detector. A portable hydrocarbon gas analyzer with associated sampling line and probe.

4.2.1 Safety. Certified as safe for operation in explosive atmospheres.

4.2.2 Range. Minimum range of 0-100 percent of the lower explosive limit (LEL) as propane.

4.2.3 Probe diameter. Sampling probe internal diameter of 0.625 cm (1/4 inch).

4.2.4 Probe length. Probe sampling line of sufficient length for easy maneuverability during testing.

4.2.5 Response time. Response time for full-scale deflection of less than 8 seconds for detector with sampling line and probe attached.

5. TEST PROCEDURE

5.1 Pressure. Place a pressure tap in the terminal, plant, or service station vapor control system, as close as possible to the connection with the truck tank. Record the pressure periodically during testing.

5.2 Calibration. Calibrate the combustible gas detector with 2.2 percent propane by volume in air for 100 percent LEL response.

5.3 Monitoring procedure. During loading or unloading, check the periphery of all potential sources of leakage of the truck tank and of the terminal, plant, or service station vapor collection system with a combustible gas detector.

5.3.1 Probe distance. The probe inlet shall be 2.5 cm from the potential leak source.

5.3.2 Probe movement. Move the probe slowly (2.0 cm/second). If there is any meter deflection at a potential leak source, move the probe to locate the point of highest meter response.

5.3.3 Probe position. As much as possible, the probe inlet shall be positioned in the path of (parallel to) the vapor flow from a leak.

5.3.4 Wind. Attempt as much as possible to block the wind from the area being monitored.

5.4 Recording. Record the highest detector reading and location for each incidence of leakage.

APPENDIX C

LEAK DETECTION PROCEDURE FOR BOTTOM-LOADED
TRUCK TANKS BY BAG CAPTURE METHOD

1. PRINCIPLE

The volume of leakage from a truck tank during loading is measured directly by placing calibrated bags over all potential sources of leakage. This quantitative monitoring procedure is an enforcement tool to confirm the continuing existence of leak-tight conditions.

2. APPLICABILITY

This method is applicable to determining the leak-tightness of truck tanks during bottom-loading without taking the truck tank out of service. The method is applicable only if the vapor control system does not create back-pressure in excess of the pressure limits of the truck tank compliance leak test. This method cannot be applied to truck tanks during top-loading, vapor collection equipment on truck tanks, or vapor control systems at terminals, plants, or service stations.

3. DEFINITIONS

3.1 Truck tank. Any container, including associated pipes and fittings, that is used for the transport of gasoline.

3.2 Compartment. A liquid-tight division of a truck tank.

3.3 Truck tank vapor collection equipment. Any piping, hoses, and devices on the truck tank used to collect and route the gasoline vapors in the tank to the bulk terminal, bulk plant, or service station vapor control system.

3.4 Vapor control system. Any piping, hoses, equipment, and devices at the bulk terminal, bulk plant, or service station, which is used to collect, store, and/or process gasoline vapors.

4. APPARATUS

4.1 Manometer. Liquid manometer, or equivalent, capable of measuring up to 6250 pascals (25 inches H_2O) gauge pressure with $\pm$ 25 pascals ($\pm$ 0.1 inches H_2O) precision.

4.2 Plastic bag. An air-tight bag, large enough to cover the truck tank's dome cover. One bag is needed for each compartment.

4.3 Bicycle tire. A bicycle innertube, or similar apparatus, modified to the appropriate diameter to fit over the truck tank's dome cover and lie flat on the top of the truck tank. One tire is needed for each compartment.

4.4 Dry gas meter.

4.5 Pump.

4.6 Calibration platform. A platform constructed such that air can be introduced through hole in the center of platform, and large enough for bicycle tire to lie flat on it.

5. BAG VOLUME CALIBRATION

5.1 Attach bag to innertube and seal with tape or other applicable sealant to ensure no leakage around interface.

5.2 Fill innertube with water.

5.3 Place bag apparatus on the calibration platform so that the air inlet is situated under the bag.

5.4 Remove air from bag.

5.5 Connect pump to dry gas meter and dry gas meter to inlet on the calibration platform.

5.6 Pump air into bag until bag is full. Record the volume from the dry gas meter and indicate volume on bag.

6. TEST PROCEDURE

6.1 Place a pressure tap in the terminal, plant, or service station vapor control system, as close as possible to the connection with the truck tank. Record the pressure periodically during testing.

6.2 During loadings, place a bag apparatus over the dome cover of each compartment in the truck tank being filled.

6.3 Remove air from bags.

6.4 Check to ensure there is a tight seal between the base of the bag apparatus and the top of the truck tank.

6.5 During loading, estimate volume of vapors collected in bags. If a bag fills before loading is complete, empty bag and resume testing.

6.6 Estimate total volume of vapors collected in the bags, making allowances in the volumes for tank domes or other equipment

6.7 Record capacity of truck tank.

6.8 Determine allowable volume of vapor leakage from truck tank as in Section 7.

6.9 Determine total loading time. This includes only time when filling is actually occurring, not breaks during the loading operation.

7. CALCULATIONS

7.1 Equation. The allowable volume of leakage from a truck tank can determined from equation 7-1.

$$V_L = (0.5V)\left(\frac{T}{t_p}\right)\left(1 - \frac{P_f}{P_i}\right) \qquad \text{(Equation 7-1)}$$

Where:

V_L = allowable volume of leakage (liters)

V = capacity volume of tank (liters)

P_i = initial pressure for the compliance pressure test (absolute units)

P_f = final pressure for the compliance pressure test (absolute units)

t_p = time limit for pressure drop for the compliance pressure test (minutes)

T = total time for loading (minutes)

7.2 Example. A 20,000 liter tank is filled to capacity in 10 minutes. The compliance pressure test has an allowable pressure drop in 5 minutes from 4500 pascals (18 inches H_2O gauge, 425 inches H_2O absolute) to 3750 pascals (15 inches H_2O gauge, 422 inches H_2O absolute). The allowable volume of leakage is 140 liters.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report provides the necessary guidance for development of regulations to limit emissions of volatile organic compounds (VOC) from gasoline tank trucks and vapor collection systems at bulk terminals, bulk plants and service stations. The intent of this guidance is to define leak tight conditions and related test procedures for vapor collection systems and tank trucks while loading and unloading gasoline at these facilities. The control approach described in this document is improved maintenance and would be enforced through the surveillance and periodic testing of leak points. This guidance includes a recommended regulation and testing procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Regulatory Guidance Gasoline Tank Trucks Gasoline Vapor Control Systems Bulk Plants Bulk Terminals Service Stations	Air Pollution Control Stationary Sources Hydrocarbon Emissions	

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Unlimited	Unclassified	30
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	Unclassified	

$$d_{av.} = \frac{1}{n} \times \sum_{i=1}^{n} d_i \qquad \text{(Eq. 2-1)}$$

Where n = number of data points

$\sum_{i=1}^{n} d_i$ = algebraic sum of the individual differences d_i

When the mean of the differences of pairs of data is calculated, be sure to correct the data for moisture, if applicable.

7.2 *Standard Deviation.* Calculate the standard deviation, Sd, as follows:

$$S_d = \left(\frac{\sum_{i=1}^{n} d_i^2 - \frac{\left(\sum_{i=1}^{n} d_i\right)^2}{n}}{n-1} \right)^{\frac{1}{2}} \qquad \text{(Eq. 2-2)}$$

7.3 *Confidence Coefficient.* Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

$$CC = t_{0.975} \times \frac{S_d}{\sqrt{n}} \qquad \text{(Eq. 2-3)}$$

Where $t_{0.975}$ = t-value

TABLE 7-1.—VALUES

n[a]	$t_{0.975}$	n[a]	$t_{0.975}$	n[a]	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

7.4 *Calibration Error.* Calculate the calibration error (Ec) of a set of data as follows:

$$\text{For carbon monoxide: } E_c = \frac{|d_{av}| + |CC|}{FS} \times 100 \text{ (Eq. 2-4)}$$

For oxygen[38]: $E_c = |d_{av}| + |CC|$

where: $|d_{av}|$ = absolute value of the mean of differences (from Equation 2-1)

$|CC|$ = absolute value of the confidence coefficient (from Equation 2-3)

FS = full scale span of monitoring system (for calculation of CO calibration error only)

7.5 *Relative Accuracy.* Calculate the relative accuracy (RA) of a set of data as follows:

$$RA = \frac{|d_{av}| + |CC|}{RM} \times 100 \text{ (Eq. 2-6)}$$

where: $|d_{av}|$ = absolute value of the mean of differences (from Equation 2-1)

$|CC|$ = absolute value of the confidence coefficient (from Equation 2-3)

RM = average value indicated by the Reference Method.

8.0 Quality Assurance

It is the responsibility of the owner/operator to assure proper calibration, maintenance, and operation of the CEMS on a continual basis. The owner/operator should establish a QA program to evaluate and monitor CEMS performance on a continual basis. The following QA guidelines are presented:

1. Conduct a daily calibration check for each monitor. Adjust the calibration if the check indicates the instrument's calibration drift exceeds the specification established in Paragraph 4.4.

2. Conduct a daily system audit. During the audit, review the calibration check data, inspect the recording system, inspect the control panel warning lights, and inspect the sample transport/interface system (e.g., flowmeters, filters), as appropriate.

3. Conduct a quarterly calibration error test at the span midpoint.

4. Repeat the entire performance specification test every second year.

9.0 Reporting

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any), summarize in tabular form, the results of the response time tests, calibration error tests, calibration drift tests, and the relative accuracy tests. Include all data sheets, calculations, charts (records of CEMS responses), cylinder gas concentration certifications, and calibration cell response certifications (if applicable), necessary to substantiate that the performance of the CEMS met the performance specifications.

10.0 References

10.1. Jahnke, james A. and G. J. Aldina, "Handbook: Continuous Air Pollution Source Monitoring Systems," U.S. Environmental Protection Agency Technology Transfer, Cincinnati, Ohio 45268, EPA–625/6–79–005, June 1979.

10.2. "Gaseous Continuous Emission Monitoring Systems—Performance Specification Guidelines for SO_2, NO_x, CO_2, O_2, and TRS." U.S. Environmental Protection Agency OAQPS/ESED, Research Triangle Park, North Carolina, 27711, EPA–450/3–82–026, October 1982.

10.3. "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume I. Principles," U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711 EPA–600/9–76–005, December 1984.

10.4. Michie, Raymond, M. Jr. et al., "Performance Test Results and Comparative Data for Designated Reference Methods for Carbon Monoxide," U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, EPA–600/S4–83–013, September 1982.

10.5. Ferguson, B.B., R.E. Lester and W. J. Mitchell, "Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, EPA–600/4–82–054, August 1982.

Appendix D: Performance Specifications for Continuous Emissions Monitoring of Total Hydrocarbons in Hazardous Waste Incinerators, Boilers and Industrial Furnaces

Note: This proposed method may be revised to allow gas conditioning including cooling to between 40 °F and 64 °F and the use of condensate traps to reduce the moisture content of sample gas entering the FID to less than 2%. The gas conditioning system, however, should not allow the

[38] For oxygen, the calibration error is expressed as % O_2 and the term $|d| + |C|$ is not divided by FS or multiplied by 100.

sample gas to be bubbled through a water column as this would remove water-soluble organic compounds. Further, although heating the sampling line and FID may be advisable to reduce operation and maintenance problems, it may not be required in the final procedure. Comments on the gas conditioning system are encouraged.

1.0 Applicabiltiy and Principle

1.1 *Applicability.* This method applies to the measurement of total hydrocarbons as a surrogate measure for the total gaseous organic concentration of the combustion gas stream. The concentration is expressed in terms of propane.

1.2 *Principle.* A gas sample is extracted from the source through a heated sample line and heated glass fiber filter to a flame ionization detector (FID). Results are reported as volume concentration equivalents of the propane.

2.0 Definitions

2.1 *Measurement System.* The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

2.1.1 *Sample Interface.* That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 *Organic Analyzer.* That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.1.3 *Data Recorder.* That portion of the system that records a permanent record of the measurement values.

2.2 *Span Value.* For most incinerators a 50 ppm propane span is appropriate. Higher span values may be necessary if propane emissions are significant. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 *Calibration Gas.* A known concentration of a gas in an appropriate diluent gas.

2.4 *Zero Drift.* The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 *Calibration Drift.* The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

2.6 *Response Time.* The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3.0 Apparatus

An acceptable measurement system includes a sample interface system, a calibration valve, gas filter and a pump preceding the analyzer. THC measurement systems are designated HOT or COLD systems based on the operating temperatures of the system. In HOT systems, all components in contact with the sample gas (probe, calibration valve, filter, and sample lines) as well as all parts of the flame ionization analyzer between the sample inlet and the flame ionization detector (FID) must be maintained between 150–175 °C. This includes the sample pump if it is located on the inlet side of the FID. A condensate trap may be installed, if necessary, to prevent any condensate entering the FID.

The essential components of the measurement system are described below:

3.1 *Organic Concentration Analyzer.* A flame ionization detector (FID) capable of meeting or exceeding the specifications in this method.

3.2 *Sample Probe.* Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 *Sample Line.* Stainless steel or Teflon [39] tubing to transport the sample gas to the analyzer. The sample line should be heated to between 150° and 175°C for a heated probe.

3.4 *Calibration Valve Assembly.* A heated three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 *Particulate Filter.* An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter must be heated.

3.6 *Recorder.* A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

4.0 Calibration and Other Gases

Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value.

4.1 *Fuel.* A 40 percent hydrogen and 60 percent helium or 40 percent hydrogen and 60 percent nitrogen gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 *Zero Gas.* High purity air with less than 0.1 parts per million by volume (ppm) of organic material methane or carbon equivalent or less than 0.1 percent of the span value, whichever is greater.

4.3 *Low-level Calibration Gas.* Propane calibration gas (in air or nitrogen) with a concentration equivalent to 20 to 30 percent of the applicable span value.

4.4 *Mid-level Calibration Gas.* Propane calibration gas (in air or nitrogen) with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 *High-level Calibration Gas.* Propane calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

5.0 Measurement System Performance Specifications

5.1 *Zero Drift.* Less than ±3 percent of the span value.

5.2 *Calibration Drift.* Less than ±3 percent of the span value.

5.3 *Calibration Error.* Less than ±5 percent of the calibration gas value.

6.0 Pretest Preparations

6.1 *Selection of Sampling Site.* The location of the sampling site is generally specified by the applicable regulation or purpose of the test, i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters upstream of the gas discharge to the atmosphere.

[39] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.2 *Location of Sample Probe.* Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 *Measurement System Preparation.* Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

6.4 *Calibration Error Test.* Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 *Response Time Test.* Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7.0 Emission Measurement Test Procedure

7.1 *Organic Measurement.* Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 *Drift Determination.* Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

8.0 Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv propane. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

9.0 Quality Assurance

It is the responsibility of the owner/operator to assure proper calibration, maintenance, and operation of the CEMS on a continual basis. The owner/operator should establish a QA program to evaluate and monitor performance on a continual basis. The following checks should routinely be done.

1. Conduct a daily calibration check for each monitor. Adjust the calibration if the check indicates the instrument's calibration drift exceeds the specification established in paragraph 5.0.

2. Conduct a daily system audit. During the audit, review the calibration check data, inspect the recording system, inspect the control panel warning lights, and inspect the sample transport/interface system (e.g., flowmeters, filters), as appropriate.

3. Conduct a quarterly calibration error test at the span midpoint.

4. Repeat the entire performance specification test every second year.

10.0 Reporting of Total Hydrocarbon Levels

THC levels from the trial burn will be reported as ppm propane. Under the health-based alternative approach to assess THC emissions, the THC levels would need to be converted to mg/s. This conversion is accomplished with the following equation:

$$\text{THC, mg/s} = (\text{THC ppm propane}) \times (\text{Stack gas Flow}) \times 2.8 \times 10^{-2}$$

Where:

- THC ppm propane is the total hydrocarbon concentration as actually measured by this method in ppm of propane,
- Stack gas flow is in dry standard cubic meters per minute measured by EPA Reference Method 5 (or Modified EPA Method 5) during the DRE trial burn, and
- 2.8×10^{-2} is a constant to account for the conversion of units, differences in FID response to various compounds and weighted average molecular weights.

11.0 References

11.1 Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, N. C. Publication No. EPA–450/2–78–041. June 1978. p. 46–54.

11.2 Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, N. C. June 1978.

11.3 Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, N. C. EMB Report No. 75–GAS–6. August 1975.

Appendix E: Feed Rate and Emission Rate Screening Limits for Metals and HCL

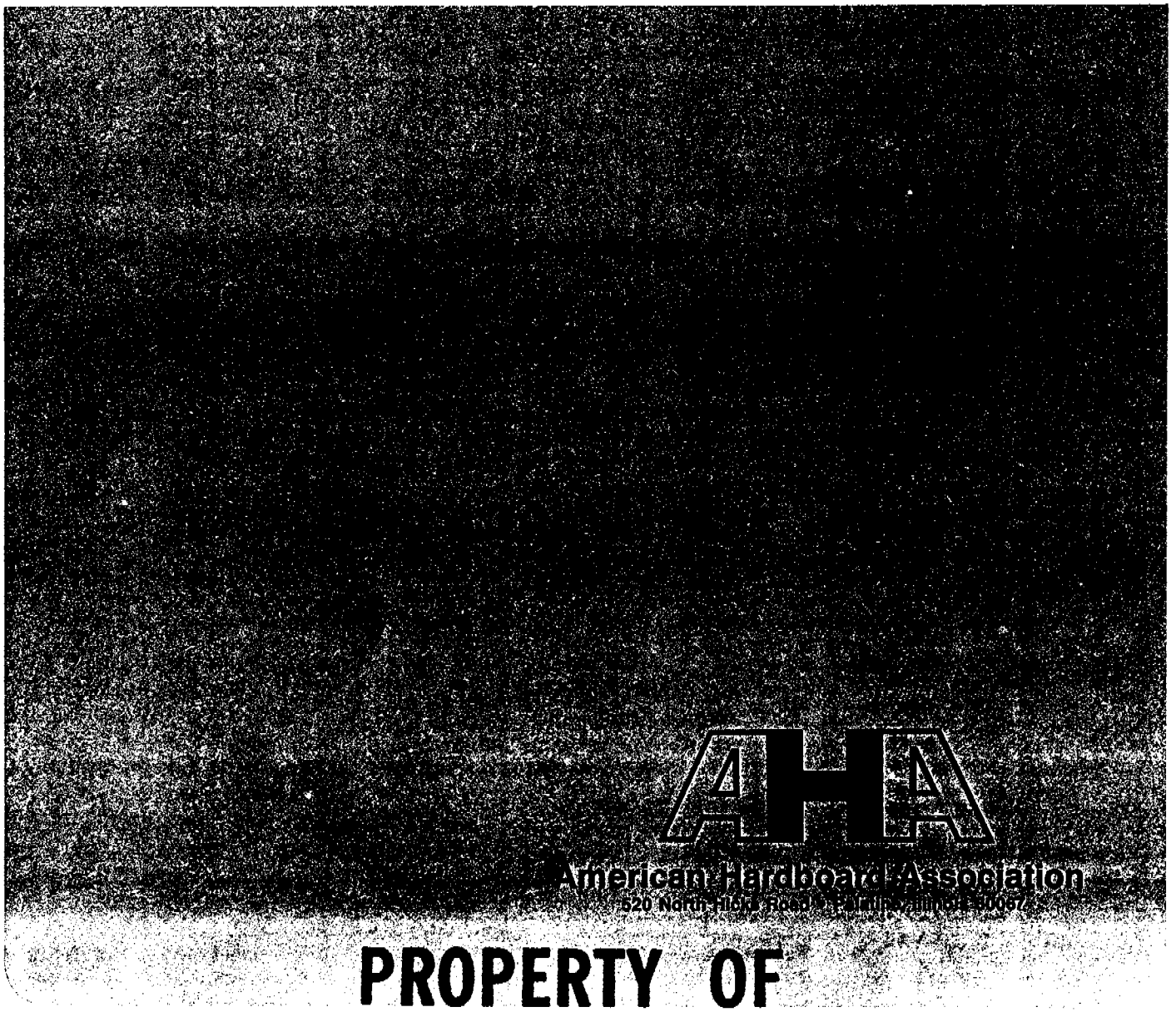
TABLE E–1.—FEED RATE SCREENING LIMITS FOR NONCARCINOGENIC METALS FOR FACILITIES IN NONCOMPLEX TERRAIN

Terrain-adjusted effective stack height	Values for urban areas					
	Antimony (lb/hr)	Barium (lb/hr)	Lead (lb/hr)	Mercury (lb/hr)	Silver (lb/hr)	Thallium (lb/hr)
4m	1.3E−01	2.2E+01	4.0E−02	1.3E−01	1.3E+00	1.3E−01
6m	1.5E−01	2.5E+01	4.5E−02	1.5E−01	1.5E+00	1.5E−01
8m	1.7E−01	2.8E+01	5.1E−02	1.7E−01	1.7E+00	1.7E−01
10m	1.9E−01	3.2E+01	5.8E−01	1.9E−01	1.9E+00	1.9E−01

ANSI/AHA A135.5-1988
Revision of ANSI/AHA A135.5-1982

American National Standard

Prefinished Hardboard Paneling



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Revision of ANSI/AHA A135.5-1982

Prefinished Hardboard Paneling

Approval Date: August 23, 1988

Abstract

This standard covers requirements and methods of test for the dimensions, squareness, edge straightness, and moisture content of prefinished hardboard paneling and for the finish of the paneling. Methods of identifying products which conform to the standard are included.

Foreword

(This Foreword is not a part of American National Standard for Prefinished Hardboard Paneling.)

This standard was originally promulgated under the procedures of the U.S. Department of Commerce National Bureau of Standards and designated as Voluntary Product Standard PS 59-73. This American National Standard is published with editorial adjustments only.

The development of this American National Standard for Prefinished Hardboard Paneling offers manufacturer, consumer, and the general public concerned with the product an effective guide developed under the consensus procedures of the American National Standards Institute.

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1. SCOPE

This standard covers requirements and methods of testing for the dimensions, squareness, edge straightness, and moisture content of prefinished hardboard paneling and for the finish of the paneling.[1]

2. REQUIREMENTS

2.1. General. Products represented as complying with this standard shall meet all of the requirements specified herein. The inspection and test procedures contained in Section 3 are to be used to determine the conformance of products to the requirements of this standard. Each producer or distributor who represents his products as conforming to this standard utilizing statistically based sampling plans which are appropriate for each particular manufacturing process but shall keep such essential records as are necessary to document with a high degree of assurance his claim that all of the requirements of this standard have been met. Additional sampling and testing of the product, as agreed upon between purchaser and seller, is not precluded by this section.

Note: Embossed products, because of their varying surfaces and patterns, require the recognition that certain adjustments and allowances are to be made in the evaluation of various physical property requirements found in this standard. Specific adjustments for embossed products have been designated wherever possible. With certain finished surface configurations, the manufacturer shall be consulted for specific adjustments in the test procedures.

2.2. Dimensions and Tolerances. The paneling shall have a nominal width of 16 inches, 4 feet, or 5 feet. The nominal length shall be from 4 through 12 feet in 1 foot increments. The nominal thicknesses shall be 1/8, 3/16, and 1/4 inch. The tolerance on the nominal length and width shall be plus or minus 1/16 inch. The tolerance on the nominal thickness shall be as specified.

Nominal Thickness	Min.– Max.
Inch	Inch
1/8 (0.125)	0.115–0.155
3/16 (0.188)	0.165–0.205
1/4 (0.250)	0.210–0.265

Thickness measurements shall be made in accordance with the applicable method in Part B of ASTM D 1037-87, Standard Methods of Evaluating the Properties of Wood-Base Fiber and Particle Panel Materials.[2]

2.3. Squareness. The length of the diagonals of the paneling shall not vary by more than 1/64 inch for each foot of length of the paneling. Opposite sides of the paneling shall not vary in length more than 1/8 inch.

2.4. Edge Straightness. The edges of the paneling shall be straight within 1/64 inch for each foot of length or width, and edges and corners shall be square cut. Edge straightness shall be determined by stretching a string or wire from one corner to the adjacent corner and measuring the widest distance between the string or wire and the panel being tested.

2.5. Moisture Content. The moisture content of the paneling shall be not less than 2.0 percent nor more than 9.0 percent and, within any one shipment, shall not vary by more than 3 percentage points as measured by the moisture content of the modulus of rupture specimens. Moisture content shall be determined in accordance with the applicable test method in Part B of ASTM D 1037-87. Since hardboard is a wood-base material, its moisture content will vary with environmental humidity conditions. When the environmental humidity conditions in the area of intended use are a critical factor, the purchaser shall specify a moisture content more restrictive than 2 to 9 percent so that fluctuation in the moisture content of the panel will be kept to a minimum.

2.6. Hardboard Substrate. The hardboard substrate of the paneling shall be manufactured primarily of interfelted ligno-cellulosic fibers which are consolidated under heat and pressure in a hot-press to a density of 31 pounds per cubic foot or greater. The finished product when tested shall have the properties

[1] *Other Standards cover: a. Basic Hardboard; b. Hardboard Siding. Physical properties of the hardboard used to manufacture prefinished paneling are set out in American National Standard A135.4-1982, "Basic Hardboard" products which conform to the requirements of this standard are included.*

Note: As an aid in correlating U.S. customary units to metric units, conversion factors for units used in this standard are given in the Appendix.

[2] *Later issues of this publication may be used providing the requirements are applicable and consistent with the issue designated. Copies are obtainable from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.*

of one of the classes listed in the American National Standard A135.4-1982 and shall have the physical properties specified therein when tested in accordance with the applicable test method in Part B of ASTM D 1037-87.

2.7. Finish. The finish of the paneling shall be either Class I or Class II as specified in Table I, and the properties of each class shall be determined in accordance with the sections of this standard indicated therein.

2.8. Workmanship. All surfaces shall be uniform in appearance throughout, and shall be as free from visible defects in the surface plane as commercially practicable when visually inspected by an individual competent in the field.

2.9. Flame Spread Index. A flame spread index for the paneling shall be determined by the Tunnel Test specified in ASTM E 84-84a, *Standard Method of Test for Surface Burning Characteristics of Building Materials,*[3] with the paneling mounted on asbestos-cement backer boards. The panels shall then be classified as follows:

Class	Flame Spread Index
I	0–25
II	26–75
III	76–200
IV	over 200

[3]*See footnote 2 on previous page*

2.10. Identification. All paneling represented as conforming to this standard shall be identified by the following method:

When requested by the purchaser the shipment or order shall be accompanied by a written certification which states that the paneling conforms to all of the requirements of this standard and identifies the producer, the flame spread index class, the finish class, the type of gloss, and the class of substrate.

3. QUALIFICATION AND TEST PROCEDURES

3.1. Abrasion Resistance. Abrasion resistance shall be determined in accordance with ASTM D *968-81, Standard Method of Test for Abrasion Resistance of Coating of Paint, Varnish, Lacquer, and Related Products by the Falling Sand Method.*[4]

3.2. Adhesion. Clean the surface of the panel with mineral spirits and allow it to dry before making a cut at least 1 inch long through the finish with a sharp razor blade. Press a piece of 3/4 inch wide flatback masking tape meeting the requirements of Type II tape in Federal Specification UU-T-106c, *Tape, Pressure-Sensitive Adhesive, Masking, Paper,*[5] firmly against the finish of the panel, perpendicular to the cut. Allow the cut to extend beyond the edges of the tape to contact the finish for a distance of at least 1 inch on each side of the cut. Allow sufficient excess tape on one side to hold the tape between the thumb and forefinger. Immediately pull the tape free in a slow and even manner at right angles to the surface. Measure the distance from the cut to where the finish ceases to be "picked up" by the tape.

Note: This test is only applicable to flat surfaces. If a textured product is to be tested, a flat area of the pattern shall be selected. Trial cuts shall be made until either the substrate becomes visible in the bottom of the cut or, in the case of intercoat adhesion, the underlying paint film becomes visible in the bottom of the cut. Disregard any cuts of improper depth, curling at the edge of the cut, or excessive chipping next to the cut.

3.3. Fade Resistance. Fade resistance shall be tested using Method 1, ASTM G 23-81, *"Recommended Practice for Operating Light-and Water-Exposure Apparatus (Carbon-Arc Type) for Exposure of Nonmetallic Materials".*[6] Gloss shall be determined in accordance with 3.4.

3.4. Gloss. Gloss shall be determined in accordance with ASTM D 523-85, *Standard Method of Test for Specular Gloss,*[6] using a glossmeter geometry of 60°.

3.5. Heat Resistance. Place a 4 by 4 inch specimen in an oven at 150°F for 24 hours.

3.6. Humidity Resistance. Place a 6 by 12 inch specimen in an atmosphere of 90 percent relative humidity and temperature of 90 plus or minus 2°F for 240 hours.

3.7. Scrape Adhesion. Scrape adhesion shall be determined in accordance with Method A of ASTM D 2197-86, *Standard Methods of Test for Adhesion of Organic Coatings.*[6]

See "Note" relative to textured products under 3.2 Adhesion.

3.8. Stain Resistance. Stain resistance shall be tested in accordance with ASTM D 1308-87, *Standard Methods of Test for Effect of Household Chemicals on Clear and Pigmented Organic Finishes,* using the Spot Test, covered method, and the following staining agents:

(a) mineral oil (U.S.P.)

(b) fresh-brewed strong coffee

Table 1
Properties of Hardboard Paneling Finishes

	Requirements		Reference to test method described in this Standard
Property	**Class I**	**Class II**	
Abrasion resistance	5 liters of sand without marring print or undercoat	3 liters of sand without marring print or undercoat	3.1
Adhesion	Less than 1/8 inch of coating "picked up"	Same as Class 1	3.2
Fade resistance	100 hours of light exposure with no loss of gloss and only a slight color change when visually inspected by an individual competent in the field	60 hours of light exposure with no loss of gloss and only a slight color change when visually inspected by an individual competent in the field	3.3
Gloss - High Medium Low	50 units and over 25 to 50 units Under 25	Same as Class I	3.4
Heat resistance	Slight color change when visually inspected by an individual competent in the field	See footnote a	3.5
Humidity resistance	No blistering, peeling, cracking, crazing, or more than a slight color change when visually inspected by an individual competent in the field	See footnote a	3.6
Scrape adhesion	6 kilograms	4 kilograms	3.7
Stain resistance	No effect using staining agents "a" through "l"	No effect using staining agents "a" through "f". Not greater than superficial effect using staining agents "g" through "l"	3.8
Steam resistance	No blistering, loosening, or separation of coating	See footnote a	3.9
Washability	No loss of print or undercoat	Same as Class I	3.10

[a]*Class II finish has limited heat, humidity, or steam resistance requirements as it is not meant to be used where these conditions are excessive such as around stoves, furnaces, showers, and bathtubs.*

Note: Physical properties of the hardboard substrate can be found in the Basic Hardboard Standard ANSI/AHA A135.4-1982.

(c) china-type marking pencil
(d) nonsmearing lipstick
(e) reconstituted lemon juice (10% citric acid by weight)
(f) carbonated cola drink
(g) household ammonia solution (10% ammonia by weight)
(h) homogenized milk
(i) alcohol (denatured) 190 proof
(j) aqueous household bleach (5.5% sodium hypochlorite by weight)
(k) nail polish remover*
(l) 1% trisodium phosphate solution (by weight)

*Nail polish remover formula:

	Volume
Butyl acetate	24%
Ethyl acetate	28%
Acetone	20%
Isopropyl alcohol	24%
Diglycol laurate	4%

The staining agent shall be allowed to stand on the test specimen for 4 hours, after which time it shall be wiped away using a damp cloth. Any stain remaining shall be gently removed by rubbing with alcohol or lacquer thinner only to the extent required to dissolve water insoluble surface stains. If 24 hours after wiping away the staining agents: (1) the specimen is free of marks and stains, then the staining agent shall be considered as having no effect; (2) any residual mark and/or stain is easily and completely removed by the light application of a mild abrasive cleaner, then the staining agent shall be considered as having only a superficial effect. Test specimens shall be examined by holding the specimen at arm's length in a vertical position under overhead white fluorescent lamps of from 75 through 100 footcandles.

[6]*See footnote 2 on previous page*

3.9. Steam Resistance. A 500 milliliter narrow-mouth Erlenmeyer flask shall be half-filled with water which shall be maintained at a mild boil at 125 ml./hour evaporation rate. A 4 inch square sample panel shall be suspended 1 inch above the mouth of the flask, with the finished face down, for 8 hours. The back and edges of the specimen shall be protected by an acrylic lacquer of at least 1 mil dry film thickness which will not soften or lose adhesion at 220°F. The specimen shall then be allowed to recover for 16 hours before grading. There shall be no more than a superficial change in appearance after testing.

3.10. Washability. The washability of the finish shall be determined in accordance with ASTM D 2486-79, *Tentative Method of Test for Scrub Resistance of Interior Latex Flat Wall Paints,*[7] incorporating the following test equipment and procedures: Use Gardner Washability Machine, Model 105-a[8], or equivalent, and a Gardner long, hog bristle brush,[8] or equivalent. Cut a specimen 6 inches by 17 inches. Determine the gloss of the coating as described in 3.4. and clamp the panel firmly in the pan of the apparatus. Soak the hog bristle brush in a 3.0 percent solution by weight of trisodium phosphate for 10 minutes and place it on the panel. Pour 10 milliliters of the same solution on the panel, adding more solution from time to time to keep the specimen moist but not soaking wet. Remove the specimen after 3,000 cycles (6,000 separate strokes), rinse with running water, wipe off with a clean sponge, and allow the specimen to dry at a temperature of 72°F plus or minus 5°F for 2 hours. Redetermine the gloss within the central 8 inches of the brush path in accordance with 3.4. and report the increase or decrease in units.

[7]*See footnote 2 on previous page*

[8]*Available from Pacific Scientific–Instruments Div., 2341 Linden Lane, Silver Spring, MD 20910. This trade name is used solely for the purpose of description and does not imply recommendation or endorsement. Other such apparatus equal in performance shall be acceptable.*

APPENDIX

"This Appendix is not a part of American National Standard for Prefinished Hardboard Paneling A135.5-1988, but is included for information purposes only."

The conversion factors and units contained in this appendix are in accordance with the International System of Units (Abbreviated SI for Systeme International d'Unites). The SI was defined and given official status by the 11th General Conference on Weight and Measures which met in Paris in October, 1960. For assistance in converting U.S. customary units to SI units, see ASTM E 380-84, *ASTM Standard Metric Practice Guide,* available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. The conversion factors for the units found in this standard are as follows:

1 inch = 25.4 millimeters
1 foot = 0.3048 meter
1 pound per square inch
= 6.894 757 × 10^3 pascals (newton/meter^2)
1 foot-candle = 10.76391 lux
$t_c = (t_f - 32)/1.8$ where:
t_c = temperature in degrees Celsius
t_f = temperature in degrees Fahrenheit