400 LEGAL REQUIREMENTS

In this chapter, the legal requirements for consumer products are presented, including the texts of the most relevant sections of the Health and Safety Code.

401 INTRODUCTION

The California Legislature passes laws, called statutes, that authorize Executive branch agencies (such as the Air Resources Board) to implement laws through regulations pursuant to the directives of the statutes.

A history of the regulation of Consumer Products is provided in Section 106 of this Manual, **including the 10 additional categories** approved by the ARB on January 9, 1992, and by the Office of Administrative Law on December 7, 1992. Regulations adopted by the Air Resources Board (ARB) are found in the California Code of Regulations (CCR). Each regulation cites specific sections of the Code as authority and as references. The codes cited by the ARB for Consumer Products regulations include applicable sections of the Health and Safety Code (HSC).

Authority to Regulate

HSC Section 41712 gives the ARB authority to regulate Consumer Products. CCR Sections 94500-94517 are also presented, in chapter 3. These regulations are in effect and important to review. Applicable authority for air pollution control districts is also cited because it may be germane, however, the **ARB has primary authority for consumer products:**

1. To routinely sample and test products for compliance,
2. To conduct related enforcement activity, and
3. To develop test methods to assure compliance with VOC limits.

District regulations for manufacturers may refer to:

1. Permits to Construct
2. Permits to Operate
3. Particulate matter
4. Visible emissions
5. Combustion emissions
6. Fugitive dust
7. Nuisances procedures
8. Breakdown and variance
9. New source performance standards(NSPS)

402 HEALTH AND SAFETY CODE

Overview of HSC Regulations

As the basis for California Air Pollution Control Laws, the texts of these relevant California HSC Sections follow, in the same order:

39000	Legislative Findings - Environment
39001	Legislative Findings - Agency Coordination
39002	Local and State Agency Responsibilities
39003	ARB Responsibilities
40000	Local/State Responsibilities
40001	Adoption and Enforcement of Rules and Regulations
40702	Adoption of Rules and Regulations
41509	No Limitation on Power to Abate Nuisance
41510	Right of Entry With Inspection Warrant
41700	No Person Shall Discharge Pollutants (Public Nuisance)
41712	Consumer Products ROC Emissions
42400	General Violations, Criminal
42400.1	Negligence, Criminal
42400.2	Document Falsification or Failure to Take Corrective Action, Criminal
42400.3	Willfully and Intentionally Emitting an Air Contaminant
42401	Violating Order of Abatement, Civil
42402	General Violations, Civil
42402.1	Negligence or Actual Injury, Civil
42402.2	Document Falsification or Failure to Take Corrective Action, Civil
42402.3	Civil Penalties
42402.5	General Violations, Administrative Civil Penalties
42403	Recovery of Civil Penalties
42404.5	Statute of Limitations for Civil Actions

Sections of the California Health and Safety Code (HSC):

39000 LEGISLATIVE FINDINGS - ENVIRONMENT

HSC Sections

The Legislature finds and declares that the people of the State of California have a primary interest in the quality of the physical environment in which they live, and that this physical environment is being degraded by the waste and refuse of civilization polluting the atmosphere, thereby creating a situation which is detrimental to the health, safety, welfare, and sense of well-being of the people of California.

39001 LEGISLATIVE FINDINGS - AGENCY COORDINATION

(HSC)

The Legislature, therefore, declares that this public interest shall be safeguarded by an intensive, coordinated state, regional, and local effort to protect and enhance the ambient air quality of the state. Since air pollution knows no political boundaries, the Legislature declares that a regional approach to the problem should be encouraged whenever possible and, to this end, the state is divided into air basins. The state should provide incentives for such regional strategies, respecting, when necessary, existing political boundaries.

39002 LOCAL AND STATE AGENCY RESPONSIBILITIES

Local and regional authorities have the primary responsibility for control of air pollution from all sources other than vehicular sources. The control of vehicular sources, except as otherwise provided in this division, shall be the responsibility of the State Air Resources Board. Except as otherwise provided in this division, including, but not limited to, Sections 41809, 41810, and 41904, local and regional authorities may establish stricter standards than those set by law or by the state board for nonvehicular sources. However, the state board shall, after holding public hearings as required in this division, undertake control activities in any area wherein it determines that the local or regional authority has failed to meet the responsibilities given to it by this division or by any other provision of law.

[Note: As stated in Section 401 "Introduction," the ARB has the primary authority given by Section 41712 to regulate consumer products.]

39003 ARB RESPONSIBILITIES

ARB's Responsibilities

The State Air Resources Board is the state agency charged with coordinating efforts to attain and maintain ambient air quality standards, to conduct research into the causes of and solution to air pollution, and to systematically attack the serious problem caused by motor vehicles, which is the major source of air pollution in many areas of the state.

40000 LOCAL/STATE RESPONSIBILITIES

The Legislature finds and declares that local and regional authorities have the primary responsibility for control of air pollution from all sources, other than emissions from motor vehicles. The control of emissions from motor vehicles, except as otherwise provided in this division, shall be the responsibility of the state board.

400 LEGAL REQUIREMENTS

40001 ADOPTION AND ENFORCEMENT OF RULES AND REGULATIONS

(HSC)

(a) Subject to the powers and duties of the state board, the districts shall adopt and enforce rules and regulations to achieve and maintain the state and federal ambient air quality standards in all areas affected by emission sources under their jurisdiction, and shall enforce all applicable provisions of state and federal law.

(b) The rules and regulations may, and at the request of the state board shall, provide for the prevention and abatement of air pollution episodes which, at intervals, cause discomfort or health risks to, or damage to property of, a significant number of persons or class of persons.

(c) Prior to adopting any rule or regulation to reduce criteria pollutants, a district shall determine that there is a problem that the proposed rule or regulation will alleviate and that the rule or regulation will promote the attainment or maintenance of state or federal ambient air quality standards.

40702 ADOPTION OF RULES AND REGULATIONS

A district shall adopt rules and regulations and do such acts as may be necessary or proper to execute the powers and duties granted to, and imposed upon, the district by this division and other statutory provisions.

41509 NO LIMITATION ON POWER TO ABATE NUISANCE

Abate Nuisances

No provision of this division, or of any order, rule, or regulation of the state board or of any district, is a limitation on:

(a) The power of any local or regional authority to declare, prohibit, or abate nuisances.

(b) The power of the Attorney General, at the request of a local or regional authority, the state board, or upon his own motion, to bring an action in the name of the people of the State of California to enjoin any pollution or nuisance.

(c) The power of a state agency in the enforcement or administration of any provision of law which it is specifically permitted or required to enforce or administer.

(d) The right of any person to maintain at any time any appropriate action for relief against any private nuisance.

41510 RIGHT OF ENTRY WITH INSPECTION WARRANT

(HSC)

For the purpose of enforcing or administering any state or local law, order, regulation, or rule relating to air pollution, the executive officer of the state board or any air pollution control officer having jurisdiction, or an authorized representative of such officer, upon presentation of his credentials or, if necessary under the circumstances, after obtaining an inspection warrant pursuant to Title 13 (commencing with Section 1822.50), Part 3 of the Code of Civil Procedure, shall have the right of entry to any premises on which an air pollution emission source is located for the purpose of inspecting such source, including securing samples of emissions therefrom, or any records required to be maintained in connection therewith by the state board or any district.

41700 NO PERSON SHALL DISCHARGE POLLUTANTS (PUBLIC NUISANCE)

Except as otherwise provided in Section 41705, no person shall discharge from any source whatsoever such quantities of air contaminants or other material which cause injury, detriment, nuisance, or annoyance to any considerable number of persons or to the public, or which endanger the comfort, repose, health, or safety of any such persons or the public, or which cause, or have a natural tendency to cause, injury or damage to business or property.

42400 GENERAL VIOLATIONS, CRIMINAL

(a) Except as otherwise provided in Section 42400.1 or 42400.2, any person who violates any provision of this part, or any order, permit, rule, or regulation of the state board or of a district, including a district hearing board, adopted pursuant to Part 1 (commencing with Section 39000) to Part 4 (commencing with Section 41500), inclusive, is guilty of a misdemeanor and is subject to a fine of not more than one thousand dollars ($1,000) or imprisonment in the county jail for not more than six months, or both.

(b) If a violation under subdivision (a) with regard to the failure to operate a vapor recovery system on a gasoline cargo tank is directly caused by the actions of an employee under the supervision of, or of any independent contractor

(HSC)

working for, any person subject to this part, the employee or independent contractor, as the case may be, causing the violation is guilty of a misdemeanor and is punishable as provided in subdivision (a). That liability shall not extend to the person employing the employee or retaining the independent contractor, unless that person is separately guilty of any action violating any provision of this part.

(c) The recovery of civil penalties pursuant to Section 42402, 42402.1, 42402.2, or 42402.3, precludes prosecution pursuant to this section for the same offense. When a district refers a violation to a prosecuting agency, the filing of a criminal complaint is grounds requiring the dismissal of any civil action brought pursuant to this article for the same offense.

(d) Each day during any portion of which a violation of subdivision (a) occurs is a separate offense.

Criminal Negligence

42400.1 NEGLIGENCE, CRIMINAL

(a) Any person who negligently emits an air contaminants in violation of any provision of this part or any rule, regulation, permit, or order of the state board or of a district pertaining to emission regulations or limitations is guilty of a misdemeanor and is subject to a fine of not more than fifteen thousand dollars ($15,000) or imprisonment in the county jail for not more than nine months, or both.

(b) Any person who owns or operates any source of air contaminant in violation of Section 41700 which causes actual injury, as defined in paragraph (2) of subdivision (d) of Section 42400.2, to the health or safety of a considerable number of persons or the public is guilty of a misdemeanor and is punishable as provided in subdivision (a).

(c) Each day during any portion of which a violation occurs is a separate offense.

(d) The recovery of civil penalties pursuant to Section 42402, 42402.1, 42402.2, or 42402.3. precludes prosecution pursuant to this section for the same offense. When a district refers a violation to a prosecuting agency, the filing of a criminal complaint is grounds requiring the dismissal of any civil action brought pursuant to this article for the same offense.

42400.2 DOCUMENT FALSIFICATION OR FAILURE TO TAKE CORRECTIVE ACTION, CRIMINAL

(HSC)

(a) Any person who emits an air contaminant in violation of any provision of this part, or any order, rule, regulation, or permit of the state board or of a district pertaining to emission regulations or limitations, and who knew of the emission and failed to take corrective action within a reasonable period of time under the circumstances, is guilty of a misdemeanor and is subject to a fine of not more than twenty-five thousand dollars ($25,000) or imprisonment in the county jail for not more than one year, or both.

Criminal Penalty $25,000 + One Year in Jail

(b) For purposes of this section, "corrective action" means the termination of the emission violation or the grant of a variance from the applicable order, rule, regulation, or permit pursuant to Article 2 (commencing with Section 42350). If a district regulation regarding process upsets or equipment breakdowns would allow continued operation of equipment which is emitting air contaminants in excess of allowable limits, compliance with that regulation is deemed to be corrective action.

Corrective Action

(c) Any person who, knowingly and with intent to deceive, falsifies any document required to be kept pursuant to any provision of this part, or any rule, regulation, permit, or order of the state board or of a district, is guilty of a misdemeanor and is punishable as provided in subdivision (a).

Falsifying Documents

(d) (1) Any person who owns or operates any source of air contaminants in violation of Section 41700 which causes actual injury to the health or safety of a considerable number of persons or the public, and who knew of the emission and failed to take corrective action within a reasonable period of time under the circumstances, is guilty of a misdemeanor and is punishable as provided in subdivision (a).

(2) As used in this subdivision, "actual injury" means any physical injury which, in the opinion of a licensed physician and surgeon, requires medical treatment involving more than a physical examination.

(e) Each day during any portion of which a violation occurs constitutes a separate offense.

Each Day

(HSC)

(f) The recovery of civil penalties pursuant to Section 42402, 42402.1, 42402.2, or 42402.3, precludes prosecution pursuant to this section for the same offense. When a district refers a violation to a prosecuting agency, the filing of a criminal complaint is grounds requiring the dismissal of any civil action brought pursuant to this article for the same offense.

42400.3 WILLFULLY AND INTENTIONALLY EMITTING AN AIR CONTAMINANT

Penalty $50,000 + One Year in Jail

(a) Any person who willfully and intentionally emits an air contaminant in violation of any provision of this part or any order, rule, regulation, or permit of the state board or of a district, pertaining to emission regulations or limitations is guilty of a misdemeanor and is subject to a fine of not more than fifty thousand dollars ($50,000) or imprisonment in the county jail for not more than one year, or both.

(b) The recovery of civil penalties pursuant to Section 42402, 42402.1, 42402.2, or 42402.3 precludes prosecution pursuant to this section for the same offense. When a district refers a violation to a prosecuting agency, the filing of a criminal complaint is grounds requiring the dismissal of any civil action brought pursuant to this article for the same offense.

42401 VIOLATING ORDER OF ABATEMENT, CIVIL

Civil Penalty $25,000 Per Day

Any person who intentionally or negligently violates any order of abatement issued by a district pursuant to Section 42450, by a hearing board pursuant to Section 42451, or by the state board pursuant to Section 41505 is liable for a civil penalty of not more than twenty-five thousand dollars ($25,000) for each day in which the violation occurs.

42402 GENERAL VIOLATIONS, CIVIL

Strict Liability $1,000

(a) Except as otherwise provided in subdivision (b) or in Section 42402.1, 42402.2, or 42402.3, any person who violates any provision of this part, or any order issued pursuant to Section 42316, or any order, permit, rule, or regulation of a district, including a district hearing board, or of the state board issued pursuant to Part 1 (commencing with Section 39000) to Part 4 (commencing with Section 41500), inclusive, is strictly liable for a civil penalty of not more than one thousand dollars ($1,000).

(HSC)

(b) (1) Any person who violates any provision of this part, any order issued pursuant to Section 42316, or any order, permit, rule, or regulation of a district, including a district hearing board, or of the state board issued pursuant to Part 1 (commencing with Section 39000) to Part 4 (commencing with Section 41500), inclusive, is liable for a civil penalty of not more than ten thousand dollars ($10,000).

Civil Penalty $10,000

(2) Where a civil penalty in excess of one thousand dollars ($1,000) for each day in which the violation occurs is sought, there is no liability under this subdivision if the person accused of the violation alleges by affirmative defense and establishes that the violation was caused by an act which was not the result of intentional or negligent conduct.

(c) Each day during any portion of which a violation occurs is a separate offense.

Each Day

42402.1 NEGLIGENCE OR ACTUAL INJURY, CIVIL

(a) Any person who negligently emits an air contaminant in violation of this part or any rule, regulation, permit, or order of the state board or of a district pertaining to emission regulations or limitations is liable for a civil penalty of not more than fifteen thousand dollars ($15,000).

Civil Penalty $15,000

(b) Any person who owns or operates any source of air contaminants in violation of Section 41700 which causes actual injury, as defined in paragraph (2) of subdivision (d) of Section 42400.2, to the health or safety of a considerable number of persons or the public is liable for a civil penalty as provided in subdivision (a).

(c) Each day during any portion of which a violation occurs is a separate offense.

Each Day

42402.2 DOCUMENT FALSIFICATION OR FAILURE TO TAKE CORRECTIVE ACTION, CIVIL

(a) Any person who emits an air contaminant in violation of any provision of this part, or any order, rule, regulation, or permit of the state board or of a district pertaining to emission regulations or limitations, and who knew of the emission and failed to take corrective action, as defined in subdivision (b) of Section 42400.2, within a reasonable period of time under the circumstances, is liable for a civil penalty, of not more than twenty-five thousand dollars ($25,000).

Civil Penalty $25,000

(HSC)

(b) Any person who, knowingly and with intent to deceive, falsifies any document required to be kept pursuant to any provision of this part, or any rule, regulation, permit, or order of the state board or of a district, is subject to the same civil penalty as provided in subdivision (a).

(c) Any person who owns or operates any source of air contaminants in violation of Section 41700 which causes actual injury, as defined in paragraph (2) of subdivision (d) of Section 42400.2, to the health or safety of a considerable number of persons or the public, and who knew of the emission and failed to take corrective action, as defined in subdivision (b), of Section 42400.2, within a reasonable period of time under the circumstances, is subject to a civil penalty as provided in subdivision (a).

(d) Each day during any portion of which a violation occurs is a separate offense.

42402.3 CIVIL PENALTIES

Penalty $50,000

Any person who willfully and intentionally emits an air contaminant in violation of any provision of this part or any order, permit, rule, or regulation of the state board, or of a district, pertaining to emission regulations or limitations, is liable for a civil penalty of not more than fifty thousand dollars ($50,000).

42402.5 GENERAL VIOLATIONS, ADMINISTRATIVE, CIVIL PENALTIES

Additional Penalties

In addition to any civil and criminal penalties prescribed under this article, a district may impose administrative civil penalties for a violation of this part, or any order, permit, rule, or regulation of the state board or of a district, including a district hearing board, adopted pursuant to Part 1 (commencing with Section 39000) to Part 4 (commencing with Section 41500), inclusive, if the district board has adopted rules and regulations specifying procedures for the imposition and amounts of these penalties. No administrative civil penalty levied pursuant to this section may exceed five hundred dollars ($500) for each violation. However, nothing in this section is intended to restrict the authority of a district to negotiate mutual settlements under any other penalty provisions of law which exceeds five hundred dollars ($500).

42403 RECOVERY OF CIVIL PENALTIES (PROCEDURES, CONSIDERATIONS)

(HSC)

(a) The civil penalties prescribed in Sections 39674, 42401, 42402, 42402.1, 42402.2, and 42402.3 shall be assessed and recovered in a civil action brought in the name of the people of the State of California by the Attorney General, by any district attorney, or by the attorney for any district in which the violation occurs in any court of competent jurisdiction.

(b) In determining the amount assessed, the court, or in reaching any settlement, the district, shall take into consideration all relevant circumstances, including, but not limited to, the following:

(1) The extent of harm caused by the violation.
(2) The nature and persistence of the violation.
(3) The length of time over which the violation occurs.
(4) The frequency of past violations.
(5) The record of maintenance.
(6) The unproven or innovative nature of the control equipment.
(7) Any action taken by the defendant, including the nature, extent, and time of response of the cleanup and construction undertaken, to mitigate the violation.
(8) The financial burden to the defendant.

42404.5 STATUTE OF LIMITATIONS FOR CIVIL ACTIONS

Statute of Limitations Begins When Discovered

Any limitation of time applicable to actions brought pursuant to Section 42403 shall not commence to run until the offense has been discovered, or could reasonably have been discovered.

NOTE: The **Business and Professions Code**, Sections 17200 and 17206 also apply to any practice which constitutes unfair competition. Please see the inspection aids at the end of Chapter 3, Compliance Assurance.

500 TEST METHODS

Consumer Products

501 INTRODUCTION

The **full text of test requirements** for antiperspirants/deodorants and consumer products is located in Sections 94506 and 94515 Title 17 CCR, incorporated into **Appendix D of this manual,** SSD Letter, pages 11, 26, and 27. Highlights of those sections and several test methods are presented here.

Which Test Shall I Use ?

For help in deciding **which test to use**, or if none of these seems appropriate for a particular product, or for information about tests being developed, you may wish to contact staff of the ARB's Monitoring and Laboratory Division: Cindy Castronovo, (916) 323-0301, or Steve Giorgi, (916) 323-0668.

Testing of antiperspirant/deodorants or consumer products for volatile organic compound (VOC) content to determine compliance with the provisions of the regulations shall be performed using **one or more of the test methods prescribed by the regulation, including but not limited to those in the following sections of this chapter:**

Section 502 Method 24-24A, Part 60, Title 40, Code of Federal Regulations, Appendix A, July 1, 1988.

Section 503 Method 18, Federal Register 48, no. 202, October 18, 1983.

Section 504 Method 1400, NIOSH Manual of Analytical Methods, Volume 1, February 1984.

Section 505 Environmental Protection Agency Method 8240 "GC/MS Method for Volatile Organics," September 1986. [December 1987]

Section 506 Demonstration through calculation of the VOCs from the manufacturer's records of the amounts of product constituents.

Alternative methods which are shown to accurately determine the concentration of VOCtion of VOCs in a subject product or its emissions, may be used upon the approval of the Executive Officer.

Other Tests

Other tests are addressed in Sections 94506 and 94515 Title 17 CCR, in Appendix D of this manual; copies may be obtained from the responsible agency: The AOAC Official Method of Analysis No. 932.11, 1990 "Babcock Method" for fragrances; ASTM D4359-90, (May 25, 1990) for liquid/solids; and SCAQMD Rule 1174, (February 28, 1991) charcoal lighter materials.

502 METHOD 24-24A
PART 60, TITLE 40
CODE OF FEDERAL REGULATIONS
APPENDIX A
JULY 1, 1988

TEST METHODS

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_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, NC 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 appropriate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_c 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.

TEST METHODS

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_{x1}).

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_{cy1}). 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_{cy2}). 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_{x2}). 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, PA 19103. It is also available for inspection at the Office of the Federal Register, Room 8401, 1100 L Street, NW., Washington, DC. 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*

Environmental Protection Agency

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content W_o using the following equation:

$$W_o = \frac{M_{x1}+M_{cy1}-M_{cy2}-M_{x2}}{M_{cy1}-M_{x1}} \qquad \text{Eq. 24A-1}$$

Report the weight fraction VOC 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:

$$V_o + \frac{\overline{W_o}\,\overline{D_c}}{\overline{D_o}} \qquad \text{Eq. 24A-2}$$

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.

503 METHOD 18
FEDERAL REGISTER 48, NO. 202
OCTOBER 18, 1983

federal register

Tuesday
October 18, 1983

Part II

Environmental Protection Agency

Standards of Performance for New Stationary Sources; Synthetic Organic Chemical Manufacturing Industry; Equipment Leaks of VOC, Reference Methods 18 and 22; Final Rule

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 60

[AD-FRL 2297-2]

Standards of Performance for New Stationary Sources; Synthetic Organic Chemical Manufacturing Industry; Equipment Leaks of VOC, Reference Methods 18 and 22

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action promulgates standards of performance for equipment leaks of Volatile Organic Compounds (VOC) in the Synthetic Organic Chemical Manufacturing Industry (SOCMI). The standards were proposed in the Federal Register on January 5, 1981 (46 FR 1136). These standards implement Section 111 of the Clean Air Act and are based on the Administrator's determination that emissions from the synthetic organic chemical manufacturing industry cause, or contribute significantly to, air pollution which may reasonably be anticipated to endanger public health or welfare. The intended effect of these standards is to require all newly constructed, modified, and reconstructed SOCMI process units to use the best demonstrated system of continuous emission reduction for equipment leaks of VOC, considering costs, nonair quality health and environmental impact and energy requirements.

DATES: Effective date: October 18, 1983.

These standards of performance become effective upon promulgation but apply to affected facilities for which construction or modification commenced after January 5, 1981.

Under Section 307(b)(1) of the Clean Air Act, judicial review of these standards of performance is available *only* by the filing of a petition for review in the U.S. Court of Appeals for the District of Columbia Circuit within 60 days of today's publication of this rule. Under Section 307(b)(2) of the Clean Air Act, the requirements that are the subject of today's notice may not be challenged later in civil or criminal proceedings brought by EPA to enforce these requirements.

The Director of the Federal Register approves the incorporation by reference of certain publications in 40 CFR effective on October 18, 1983.

ADDRESSES: *Background Information Documents.* The background information document (BID) for the promulgated standards may be obtained from the U.S. EPA Library (MD-35), Research Triangle Park, North Carolina 27711, telephone number (919) 541-2777. Please refer to "Equipment Leaks of VOC in Synthetic Organic Chemicals Manufacturing Industry—Background Information for Promulgated Standards of Performance" (EPA-450/3-80-033b). The BID contains (1) a summary of all the public comments made on the proposed standards and EPA's responses to the comments, (2) a summary of the changes made to the standards since proposal, and (3) the final Environmental Impact Statement which summarizes the impacts of the promulgated standards. The BID for the proposed standards may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161. Please refer to "VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry—Background Information for Proposed Standards," EPA-450/3-80-033b (NTIS PB81-152167). The additional information document (AID) describing emissions, emission reductions, and costs related to equipment leaks of VOC may also be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161. Please refer to "Fugitive Emission Sources of Organic Compounds—Additional Information on Emissions, Emission Reductions, and Costs," EPA-450/3-82-010 (NTIS PB82-217126).

Docket. A docket, number A-79-32, containing information considered by EPA in development of the promulgated standards, is available for public inspection between 8:00 a.m. and 4:00 p.m., Monday through Friday, at EPA's Central Docket Section (A-130), West Tower Lobby, Gallery 1, 401 M Street, SW., Washington, D.C. 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Mr. Fred Dimmick, Standards Development Branch, Emission Standards and Engineering Division (MD-13), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone (919) 541-5578.

SUPPLEMENTARY INFORMATION:

Summary of Standards

Standards of performance for new sources established under Section 111 of the Clean Air Act reflect:

> . . . application of the best technological system of continuous emission reduction which (taking into consideration the cost of achieving such emission reduction, and any nonair quality health and environmental impact and energy requirements) the Administrator determines has been adequately demonstrated [Section 111(a)(1)].

As prescribed by Section 111 of the Clean Air Act, promulgation of these standards was preceded by the Administrator's determination (40 CFR 60.16, 44 FR 49222, dated August 21, 1979) that these sources contribute significantly to air pollution which may reasonably be anticipated to endanger public health or welfare.

Standards of performance for equipment leaks of volatile organic compounds (VOC) in the synthetic organic chemical manufacturing industry (SOCMI) were proposed on January 5, 1981 (46 FR 1136).[1] The promulgated standards apply to specific equipment with the potential to leak VOC within process units operated to produce one or more of the organic chemicals listed in the standards. The equipment covered by the standards and grouped in a process unit are designated as the "affected facility" for determining applicability of the standards. A process unit is a group of equipment that can be used independently, if sufficient raw material and product storage capacity could be supplied, to produce one or more chemicals. Process units used to produce the chemicals covered by the standards may involve chemical synthesis, bilological synthesis, other processing, or physical operations, such as separation. A plant may be composed of one or more process units.

Valves, pumps, compressors, pressure relief devices, sampling systems, and open-ended lines in VOC services (that is, containing 10 percent or more VOC by weight) are the equipment covered by the standards. The standards require (1) a leak detection and repair program for valves in gas/vapor and light liquid service and pumps in light liquid service; (2) equipment for compressors, sampling systems, and open-ended lines; (3) no detectable emissions (500 ppm as determined by Reference Method 21) for pressure relief devices in gas/vapor sesrvice during normal operation. In response to comments on the proposed standards, EPA is exempting from the

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[1] The proposed standards referred to fugitive emission sources of VOC as the air pollution emission points covered by the standards. The terminology fugitive emission sources can be confusing. The standards apply to equipment with the potential to leak VOC and, therefore, the promulgated standards refer to equipment leaks of VOC as the air pollution emission points covered by the standards. The Priority List (40 CFR 60.16) specifies fugitive emission sources within the SOCMI source category. Equipment leaks of VOC are included in fugitive emision sources for the purpose of the Priority List.

standards facilities producing less than 1,000 megagrams (Mg) of SOCMI chemicals per year, facilities processing only heavy liquids or solids, and facilities producing beverage alcohol. In addition, the final standards provide a procedure for determining the equivalency of alternative control measures similar to the proposed procedure.

Standards for Valves. The standards for valves have not substantially changed since proposal. They are based on a leak detection and repair program that requires (1) monthly monitoring for valves in gas/vapor and light liquid service, (2) an intitial attempt at repairing these valves within 5 days after detection of a leak, (3) repair of leaking valves within 15 days after detection of the leak unless repair would require a process unit shutdown, and (4) repair of valves during the next process unit shutdown after repair is delayed until a process unit shutdown. Valves found not to leak for 2 successive months can be monitored quarterly until leaks are deteted. Monitoring of equipment to detect leaks is conducted in accordance with Reference Method 21 and a leak is defined as a measured organic concentration equal to or greater than 10,000 parts per million by volume (ppmv).

Two alternative standards have been provided for valves in gas/vapor and light liquid service in the final standards. These alternatives are (1) a limit of 2 percent of valves which may be leaking at any one time and (2) a skip-period leak detection and repair program for process units achieving less than 2 percent of their valves leaking. These alternative standards, although slightly different than the alternative standards included in the proposed standards, establish standards for owners and operators who design and operate low-peak process units. For low-leak process units, the costs of the monthly leak detection and repair program is unreasonably high in comparison to the emission reductions.

Standards for Pumps. The final standards include a leak detection and repair program that requires (1) monthly monitoring of pumps in light liquid service, (2) weekly visual inspections of the seals on pumps in light liquid service, (3) an attempt at repairing a pump within 5 days after detection of a leak, and (4) repair of a leaking pump within 15 days after detection of a seal failure or leak unless repair would require a process unit shutdown. Pumps that have repair delayed until a process unit shutdown must be repaired during the next process unit shutdown. If a pump cannot be repaired without the use of dual seals and barrier fluid systems or vented seal areas, a delay of repair is allowed to install the equipment. In this case, an owner or operator must install the equipment as soon as practicable but may take no longer than 6 months.

The proposed standards required the use of equipment. The use of equipment reduces more emissions than the monthly leak detection and repair program. Even though the standards have changed, pumps in light liquid service alternately could use the equipment specified in the proposed standards and, thereby, not be required to implement the monthly leak detection and repair program.

Standards for Compressors. The standards have not changed since proposal and require compressors to be equipped with seals having a barrier fluid system that prevents leakage of the process fluid to the atmosphere. The system must: (1) Use a barrier fluid that is something other than a light liquid or gaseous VOC; (2) either operate at a pressure greater than the compressor seal area pressure, or be equipped with a barrier fluid degassing reservoir connected by a closed vent system to a control device; and (3) be equipped with a sensor so that seal failures may be detected. When seal failure is detected, repair is required within 15 days unless repair would require a process unit shutdown. An initial attempt at repair is required within 5 days. If a compressor is equipped with a closed vent system to transport leakage from the seal to a control device, it is exempt from the above requirements.

Certain reciprocating compressors covered by virtue of modification and reconstruction may be exempt from the requirements for compressors. Some existing compressors are not designed to use the equipment required by the standards. For these compressors either new compressor or a new distance-piece would be required before compliance with the standards could be achieved. The cost impact of installing the required control equipment on these existing compressors is unreasonable. These compressors will be exempt from the standards until they are replaced by new compressors or the distance pieces are replaced.

Standards for Sampling Connections. The standards require that VOC purged from sampling connections be recycled to the process by a closed sampling loop or that these VOC be collected in a closed collection system for recycle or disposal without VOC emission to atmosphere. In-situ sampling systems are exempt from these requirements. These standards have not changed since proposal.

Standards for Open-ended Lines. The standards require that: (1) Open-ended lines be sealed with a second valve, cap, blind flange or plug except when the open-ended line is in use; and (2) if a second valve is used, the valve on the process side be closed first to avoid trapping VOC between the valves. These standards have not changed since proposal.

Standards for Pressure Relief Devices. The standards require that: (1) Pressure relief devices have "no detectable emissions" of VOC except in cases of overpressure relief; and (2) after each overpressure relief, pressure relief devices be returned to a state of no detectable emissions within 5 days. These standards have not changed since proposal. As noted in the preamble to the proposed standards, pressure relief devices are one of the few fugitive emission sources for which a performance standard can be established. There are a variety of alternative ways of complying with this standard. "No detectable emissions" of VOC, in this case, means 500 ppm or less above the background level as measured by Reference Method 21.

Standards for Control Devices. The standards include requirements for control devices used in conjunction with control of equipment leaks. The standards require: (1) That vapor recovery systems be designed and operated for at least 95 percent control; (2) that enclosed combustion devices be designed and operated to provide a minimum residence time of 0.75 seconds at a minimum temperature of 816°C or to achieve 95 percent reduction; and (3) that flares (a) be operated with no assist or with air or steam assist, (b) be designed and operated with no visible emissions except for periods of time not to exceed 5 minutes in any 2-hour period, (c) be operated with a flame present, and (d) meet other operational requirements including maximum exit gas velocities and minimum heat content values. Flares have been added to the approaches for achieving the standards since proposal. Otherwise, the standards for control devices have not changed since proposal.

Miscellaneous Provisions. Flanges, pressure relief devices in liquid service, equipment operating at subatmospheric pressures, and all equipment components in "heavy liquid" VOC service are excluded from the routine monitoring requirements of the proposed standards. Heavy liquids are defined as VOC liquids with vapor pressures less than 0.3 kilopascals at 20°C. Even though the standards do not require monitoring these equipment for leaks, the standards require VOC leaks which are visually or otherwise detected from these equipment to be repaired within 15 days if a leak is confirmed using Reference Method 21. This provision improves current industry housekeeping practices for these pieces of equipment.

Under Section 111(h)(3), any person may request the Administrator to permit the use of an alternative means of emission limitation instead of a design, equipment, work practice or operational standard. The Administrator will permit the use of such alternative means if the Administrator determines, after notice and opportunity for a public hearing, that it will achieve emission reductions at least equivalent to those required by the design, equipment, work practice or operational standards. The permission will take the form of an amendment to the appropriate standards.

Compliance with the leak detection and repair program and equipment requirements will be assessed through semiannual reports, review of records, and by inspection. The semiannual reports provide a summary of the data recorded on leak detection and repair of valves, pumps, and of other equipment types. In response to public comments, requirements for routine reporting were reduced from quarterly to semiannual reporting. Notifications are still required as described in the General Provisions for new source standards (40 CFR 60.7).

The semiannual reports may be waived for affected facilities in States where the regulatory program has been delegated, if EPA, in the course of delegating such authority, approves reporting requirements or an alternative means of source surveillance adopted by the State. In these cases, such sources would be required to comply with the requirements adopted by the State.

Records of leak detection, repair attempts, and maintenance for equipment leaks of VOC are required by the standards. These records, along with semiannual reporting and plant inspections, will be used to enforce the standards. The records remain essentially the same as those in the proposed standards. Some changes have occurred because the requirements for the equipment covered by the standards have changed. In addition, EPA has made it clear that an owner or operator may keep the records for several affected facilities at one location in a plant rather than at each process unit.

Miscellaneous Actions. The General Provisions of Part 60 are being revised to provide technical amendments to the provisions in 40 CFR 60.7, 60.11, and 60.17. Also, Reference Method 18 is being added to Appendix A of Part 60 and Reference Method 22 is being revised. These methods will be used to determine compliance with the requirements for flares.

Summary of Impacts

Emission Reductions. The standards of performance will reduce equipment leaks of VOC from newly constructed, modified, and reconstructed process units in SOCMI by approximately 56 percent in comparison to those emissions that would result in the absence of the standards. The standards will cover about 830 newly constructed, modified, and reconstructed sources in 1985. The standards will reduce the emissions associated with current industry practices from approximately 83,000 to 37,000 Mg in 1985 (that is, 91,000 to 41,000 tons) for newly constructed, reconstructed, and modified process units.

Cost and Economic Impacts. The cost and economic impacts of the standards are reasonable. The standards will require an industry-wide capital investment over the 5-year period from 1981 to 1986 of approximately $44 million for those facilities which are newly constructed, reconstructed, or modified. The industry-wide net annualized cost will be about $14.6 million in 1985. This net annualized cost includes a credit resulting from "recovered" emissions. The costs will be distributed among 830 facilities affected during the 5-year period. Industry-wide price increases are not expected to result from these standards.

Other Impacts. The standards of performance will not increase the energy usage of SOCMI process units. In general, the controls required by the standards do not require energy. Futhermore, the effect of the standards will be to increase efficiency of raw material usage so that a net positive energy impact will result. Implementation of the standards will have no impact on solid waste within SOCMI. In contrast, the standards could also cause a small positive impact on water quality by containment of potential liquid leaks. The recordkeeping and reporting requirements will require an average of 65 industry person years annually for the years of 1983 and 1984.

The environmental, energy, and economic impacts are discussed in greater detail in the background information document for the promulgated standards. [See the ADDRESSES section of this preamble.]

Public Participation

Prior to proposal of the standards, interested parties were advised by public notice in the Federal Register (45 FR 18474, March 21, 1980) of a meeting of the National Air Pollution Control Techniques Advisory Committee to discuss the standards for equipment leaks of VOC in SOCMI recommended for proposal. This meeting was held on April 16, 1980. The meeting was open to the public, and each attendee was given an opportunity to comment on the standards recommended for proposal. The standards were proposed in the Federal Register on January 5, 1981 (46 FR 1136). The preamble to the proposed standards discussed the availability of the background information document for the proposed standards which described in detail the regulatory alternatives considered and the impacts of those alternatives.

Public comments were solicited at the time of proposal and, when requested, copies of the BID were distributed to interested parties. To provide interested persons the opportunity for oral presentation of data, views, or arguments concerning the proposed standards, a public hearing was held on March 3, 1981, at Research Triangle Park, North Carolina. The hearing was open to the public and each attendee was given an opportunity to comment on the proposed standards. The public comment period was from January 5, 1981 to July 31, 1981. The comment period was extended to July 31, 1981, to allow interested parties to comment on several studies performed by EPA's Office of Research and Development which became available at proposal or after proposal. Fifty-six comment letters were received and 9 interested parties testified at the public hearing concerning issues relative to the proposed standards of performance for equipment leaks of VOC from SOCMI units.

EPA published an Additional Information Document (AID) in April of 1982. The AID contains a technical discussion of methodologies and estimates of emissions, emission reductions, and costs associated with control of equipment leaks of VOC. A notice of the availability of the AID and a request for comments on the AID was published in the Federal Register on May 7, 1982 (47 FR 19724). Fourteen letters were received containing comments on the AID.

Comments on the proposed standards and on the AID have been carefully considered and, where determined to be appropriate by the Administrator, changes have been made in the proposed standards.

Significant Comments and Changes to the Proposed Standards

Comments on the proposed standards were received from industry, State and local air pollution control agencies, trade associations, and environmental groups. A detailed discussion of these comments and responses can be found in the BID for the promulgated standards. [See the ADDRESSES section of this preamble.] The comments and responses in the BID serve as the basis for the revisions which have been made to the standards between proposal and promulgation. Major changes made in the standards since proposal are indicated in the "Summary of Standards" section of the preamble. The major comments and responses are summarized in the next sections of this preamble. The comments and responses in this preamble have been combined into the following areas: Need for Standards, Selection of the Final Standards, Control Technology—Use of Flares, and Test Methods and Monitoring.

Need for Standards

Comment 1: Commenters questioned whether standards of performance are needed for SOCMI because SOCMI equipment leaks emit small quantities of VOC.

Response 1: SOCMI is a significant source of VOC emissions and equipment leaks of VOC are one of the primary contributors to the total VOC emissions from SOCMI. EPA estimates that 540,000 megagrams per year (Mg/yr) of VOC are emitted from all sources in SOCMI (docket item IV–B–24). This estimate of emissions is based on detailed studies of individual process source types including air oxidation processes, distillation operations, storage operations, carrier gas processes, equipment leaks, and secondary sources. Five hundred forty thousand Mg/yr is a significant quantity of VOC to be emitted as air pollution.

The significance of SOCMI VOC emissions is reflected in the Priority List, 40 CFR 60.16. Of the 59 major source categories on this list for which standards of performance were to be promulgated by 1982, the SOCMI source category ranked first. The Priority List consists of categories of air pollution sources that, in EPA's judgment, cause or contribute significantly to air pollution which may reasonably be anticipated to endanger public health or welfare. In developing the Priority List, major source categories were ranked according to three criteria specified in Section 111(f) of the Act: (1) The quantity of emissions from each source category, (2) the extent to which each pollutant endangers public health or welfare, and (3) the mobility and competitive nature of each stationary source category. Commenters have not presented any new information which would change the decision to list SOCMI on the Priority List.

Based on comments and information received during this rulemaking, EPA has revised the estimates of emissions of VOC from equipment leaks within SOCMI since the standards were proposed. The current estimate of 540,000 Mg/yr includes the revised emission estimates. Even with the revised emission estimates, the Administrator still considers SOCMI a source category that causes or contributes significantly to air pollution which may reasonably be anticipated to endanger public health or welfare. It should be noted that because VOC emissions come from many, diverse source categories, each source category contributes a relatively small percentage to the large overall total emissions. Even though SOCMI may represent a small percentage of total VOC emissions, the magnitude of emissions from SOCMI is significant.

Since SOCMI is on the Priority List as a significant contributor to air pollution under section 111(f), standards of performance are required to be promulgated for those new sources within this source category for which the EPA can identify the best demonstrated technology (considering costs). EPA has identified several alternative systems of control capable of achieving additional emission reduction at reasonable cost at SOCMI sources. It is, therefore, reasonable for EPA to establish standards for these sources.

In addition, standards of performance have other benefits in addition to achieving emissions reductions. Standards of performance establish a degree of national uniformity to air pollution standards, and therefore, preclude situations in which some States may attract new industries as a result of having relaxed standards relative to other States. Further, standards of performance provide documentation that reduces uncertainty in evaluations of available control technology. This documentation includes identification and comprehensive analyses of alternative emission control technologies, development of associated costs, evaluation and verification of applicable emission test methods, and identification of specific emission limits achievable with alternate technologies. This documentation also provides an economic analysis that reveals the affordability of controls in a study of the economic impact of controls on an industry.

Comment 2: Commenters stated that there is no need for the standards because emissions of VOC in SOCMI are adequately controlled by other regulations, specifically:

(a) National ambient air quality standards (NAAQS) and the State implementation plans (SIP) to implement these standards;

(b) National emission standards for hazardous air pollutants (NESHAP); and

(c) Occupational safety and health standards under the Occupational Safety and Health Act (OSHA).

Response 2: Standards of performance required by Section 111 play a unique role under the Clean Air Act. The main purpose of standards of performance is to require new sources, wherever located, to reduce emissions to the level achievable by the *best* technological system of continuous emission reduction considering the cost of achieving such emission reduction, any nonair quality health and environmental impact, and energy requirements [(Section 111(a)(1))]. Congress recognized that establishing such standards would minimize increases in air pollution from new sources, thereby improving air quality as the Nation's industrial base is replaced over the long term. The role of standards of performance in achieving the goals set forth in the Clean Air Act is distinct from that of other regulations.

(a) *NAAQS and SIP:* Reasonably available control technology (RACT) requirements apply to existing sources and are based on SIP's developed for the purpose of attaining the NAAQS. Standards of performance supplement the role played by RACT and the two types of control do not conflict. In the few areas where RACT-level control is already in place, the environmental impact of standards of performance will be smaller than calculated. EPA has determined, however, that existing RACT-level facilities that become subject to the standards of performance (e.g., through modification) will be achieving additional emission reductions at reasonable costs. In most areas of the Nation, RACT-level controls are not in place and the standards fulfill their role of preventing new air pollution from developing as the Nation's industrial base is replaced.

(b) *NESHAP:* NESHAP, as mandated under Section 112 of the Clean Air Act, are distinctly separate from NAAQS or new source standards of performance. NESHAP are developed to control pollutants that are hazardous because they are carcinogens or the cause of other serious diseases. Some of the individual SOCMI chemicals have been identified as hazardous air pollutants and some SOCMI units may be affected by NESHAP regulations. However, SOCMI VOC emissions as a class have not been identified as hazardous pollutants, and therefore, are not subject to NESHAP.

(c) *OSHA:* Many of the chemicals covered by the standards are also listed in Table Z-1, Toxic and Hazardous Substances, in the general provisions for OSHA (29 CFR 1910.1000), and some of these chemicals are also covered by more specific health standards under OSHA. As a consequence, the SOCMI standards and the OSHA standards may affect the same equipment in VOC service. However, this possibility does not negate the need for the standards.

The SOCMI standards of performance serve to limit mass emission rates directly; OSHA standards for toxic chemicals generally do not. Under OSHA, control of emission sources may include substitution with less hazardous materials, process modification, worker rotation, process or worker isolation, ventilation controls, or modification of work practices. These controls reduce occupational exposures, but they do not necessarily reduce the mass rate of VOC emissions to the atmosphere. Furthermore, OSHA regulations would require control to different concentration levels, depending on the toxicity of a specific chemical, while the standards of performance require emission control for all VOC. Relying on indirect controls that may or may not reduce emissions that would degrade air quality would be an unreasonable approach to reducing emissions of VOC.

Comment 3: Commenters claimed that the standards are not needed to protect the public health and welfare. These commenters noted that the ambient air quality standard for ozone which is set to protect the public has recently been raised. The commenters continued by adding that, because most of the country is in compliance with the ozone standard, the public health and welfare is already protected and, therefore, the standards of performance are not needed.

Response 3: Standards of performance are not directly designed to achieve the ambient air quality goals. Their overriding purpose is rather to minimize emissions at all new and modified sources, wherever they are located, to prevent new pollution problems from developing, and to enhance air quality as the Nation's industrial base is replaced. Thus, the standards may not bear directly on current attainment or nonattainment of NAAQS for ozone. Nonetheless, they do make room for future industrial growth while preventing future air quality problems—complementing the prevention of significant deterioration (PSD) and non-attainment rules as a means of achieving and maintaining the NAAQS. Clearly, residents in both attainment and non-attainment areas will ultimately benefit from such standards.

Basis for the Final Standards

Comment: Several commenters questioned EPA's selection of the proposed standards. The commenters felt that other regulatory options would have been more cost-effective and, therefore, should have been chosen. Referring to the regulatory alternatives presented in EPA-450/3-80-033a, some commenters recommended selection of regulatory alternatives II or III instead of regulatory alternative IV. Some commenters also suggested that EPA select the final standards after considering the cost effectiveness of each control technique for each piece of equipment covered by the standards. Other commenters recommended selection of regulatory alternative IV.

Response: Section 111 of the Clean Air Act, as amended, requires that standards of performance be based on the best system of continuous emission reduction that has been adequately demonstrated, considering costs, nonair quality health and environmental impacts and energy requirements. The control techniques for equipment leaks of VOC have been adequately demonstrated. The nonair quality health and environmental impacts associated with implementaion of the standards are positive.

Since proposal, EPA has decided to accept the suggestions of the commenters and focus further on cost effectiveness as the basis for the selection of final standards. In using cost effectiveness of individual control techniques as the basis for selection, the regulatory alternative framework presented in the BID for the proposed standards is no longer pertinent and is not presented. The control strategies represented by the regulatory alternatives were, however, considered in the selection of the final standards. In choosing among the control techniques for each type of equipment covered by the standards, EPA first considered their relative cost effectiveness. Then, for the control techniques which were selected as the most effective with reasonable costs, EPA considered the economic impact on the industry of these control techniques.

Cost-Effectiveness Considerations. EPA analyzed the annualized cost of controlling VOC emissions and the resultant VOC reduction for each alternative control technique. The control costs per megagram of VOC reduced for medium-sized process units are presented in Table 1 for each equipment type covered by the standards. These costs do not represent the actual amounts of money spent at any particular plant site. The cost of VOC emission reduction systems will vary according to the chemical product being produced, production equipment, plant layout, geographic location, and company preferences and policies. However, these costs and emission reductions are considered typical of control techniques for leaking equipment within SOCMI units and can be used in selecting the level of control to be required by the standards.

Pressure Relief Devices. The annualized costs and VOC emission reductions achieved for monthly and quarterly leak detection and repair programs and for the use of control equipment (rupture disks) were determined for pressure relief devices in gas service. As Table 1 shows, both the quarterly and monthly leak detection and repair programs are less expensive than installation of rupture disks.

TABLE 1.—CONTROL COSTS PER MEGAGRAM OF VOC REDUCED [a]

Equipment type and control technique [b]	Emission reduction (Mg/yr)	Average $/Mg [c]	Incremental $/Mg [d]
Pressure relief devices:			
Quarterly leak detection and repair	4.4	(e)	
Monthly leak detection and repair	5.1	(e)	500
Rupture disks [f]	10.0	510	1,200
Compressors: *Controlled degassing vents* [f]	4.0	(e)	(e)
Open-ended lines: *Caps on open-ended lines* [f]	6.2	400	400
Sampling Systems: *Closed purge sampling* [f]	3.4	590	590
Valves:			
Semi-annual leak detection and repair	17.1	(e)	
Quarterly repair leak detection and repair	26.9	(e)	(e)
Monthly leak detection and repair [f]	33.6	62	480
Pumps:			
Quarterly leak detection and repair	4.1	1,200	
Monthly leak detection and repair [f]	7.6	610	(e)

TABLE 1.—CONTROL COSTS PER MEGAGRAM OF VOC REDUCED [a]—Continued

Equipment type and control technique[b]	Emission reduction (Mg/yr)	Average $/Mg[c]	Incremental $/Mg[d]
Dual mechanical seal systems vented to a flare	12.6	2,300	5,600

[a] Costs and emission reductions based on equipment counts in Model Unit B. See Section 3.2 of the BID for the promulgated standards.

[b] Further discussion of control techniques can be found in Section 4 of the BID for the promulgated standards.

[c] Average dollars per megagram (cost effectiveness) = (net annualized cost per component) + (annual VOC emission reduction per component).

[d] Incremental dollars per megagram = (net annualized cost of the control technique) – net annualized cost of the next less restrictive control technique + (annual emission reduction of control technique – annual emission reduction of the next less restrictive control technique).

[e] Values are savings with the total savings indicated in the text.

[f] Control technique selected as the basis for the standard.

Leak detection and repair programs result in average credits of $240/Mg and $150/Mg of VOC for quarterly and monthly programs, respectively. A monthly leak detection and repair program achieves an additional 0.7 Mg/yr emission reduction for medium-sized process units at an incremental cost of $500/Mg compared to a quarterly leak detection and repair program. Rupture disks achieve an additional 4.9 Mg/yr emission reduction at an incremental cost of $1,200/Mg compared to a monthly leak detection and repair program. However, EPA is establishing a performance standard (as indicated by no detectable emission limit) allowing a variety of alternative ways to complying with the standard. Because EPA used conservative assumptions in making this incremental cost calculation, the $1,200/Mg incremental cost of achieving this 4.9 Mg/yr of emission reduction is more than what many process units would experience. Thus, a no detectable emission limit was selected as the basis for the pressure relief device standard.

Compressors. Only one control technique can be considered for compressor seals: the installation of control equipment such as barrier fluid systems. If a compressor is found leaking, the repair procedure would be the installation of control equipment. Because compressors are not generally spared, repair would be delayed until the next turnaround, thereby reducing the effectiveness of a leak detection and repair program to essentially zero. The installation of control equipment results in a savings ($100/Mg of VOC), indicating that the the value of product retained by controlling the barrier fluid system exceeds the cost of the control equipment. This cost is reasonable and, therefore, control equipment was selected as the basis for the standard for compressors.

Open-ended Lines and Sampling Systems. EPA considered caps or closures as the control technique for open-ended lines. Caps and closures are in wide-spread use in SOCMI and are expected to be used even more frequently in new SOCMI units. The cost and emission reduction presented in Table 1 are the cost and emission reduction which would be realized for an open-ended line that is not controlled. The $400/Mg cost for controlling emissions of VOC from open-ended lines is reasonable.

EPA considered closed purge sampling as the control technique for sampling systems. Closed purge systems are becoming increasingly common in the chemical industry. The $590/Mg cost for controlling emissions of VOC from sampling systems is reasonable.

Valve. Several leak detection and repair programs were considered for valves. The programs differed in the monitoring frequency which would be implemented. As Table 1 shows, the quarterly monitoring program results in savings ($41/Mg of VOC on the average). This occurs because the value of the recovered VOC is greater than the cost to implement the quarterly monitoring program. However, the largest emission reduction is associated with the monthly program at an average cost of $62/Mg. Furthermore, the incremental cost per Mg VOC emissions reduced for the monthly program is $510/Mg with an incremental emission reduction of 6.7 Mg/yr for a medium-sized process unit. EPA considers these costs to be reasonable. Therefore, EPA selected a monthly leak detection and repair program as the basis for the standard for valves.

Pumps. The control costs incurred for each megagram of VOC emissions reduced were determined for two leak detection and repair programs and for the use of dual mechanical seals with controlled degassing vents. Both leak detection and repair programs incur lower costs than the costs which would be incurred with equipment installation. The lowest average and incremental costs per Mg are associated with a monthly leak detection and repair program. The monthly program achieves a higher degree of control than the quarterly program, but it achieves a lower degree of control than installation of contol equipment. However, even though control equipment provides for the greatest amount of VOC reduction, the $5,600/Mg incremental costs to obtain the additional 5 Mg/yr are judged to be unreasonably high. Because the costs for equipment are unreasonably high, monthly leak detection and repair was selected as the basis for the standard for pumps.

Economic Impact Considerations. An economic analysis was performed which evaluated the economic impacts of the selected standards. The results of that analysis are presented in detail in the BID for the promulgated standards. As summarized in the Summary of the Impacts of the Standards section of this preamble, the industry-wide net annualized cost will be about $14.6 million in 1985. This cost is not expected to result in industry-wide price increases. These impacts are reasonable.

Control Technology—Use of Flares

Comment: Several commenters expressed the desire to use flares as alternatives to enclosed incinerators or vapor recovery systems. The comments focused on: (1) Data base support of low flare efficiency, (2) high efficiencies reported for flares on refinery gases, (3) alternative flare designs for low flow applications, (4) safety considerations in choosing control systems, and (5) equivalency to other combustion devices.

Response: The control technology for controlling equipment leaks of VOC from SOCMI is discussed in the background information documents (BID's) for the proposed standards and for the promulgated standards. [See ADDRESSES section of this preamble.] In the BID for the proposed standards, EPA discussed the control technology that can be used in complying with the standards. As discussed in the BID for the promulgated standards, EPA reviewed the comments received on the control technology for controlling equipment leaks and found nothing which would alter the original judgments concerning these control techniques except with regard to the control efficiency associated with flares used in SOCMI.

The use of flares was reconsidered by EPA. Flares are used widely in SOCMI for handling emergency releases from process units and for combusting streams from continuous vents. Since the flare efficiency estimate at proposal was made, further actual flare measurement results have become available, most notably from the Chemical Manufacturers Association

(CMA)-EPA study. In the CMA-EPA study, flares were investigated over a wide range of exit velocity, composition, and flare gas heat content conditions. After review of available flare efficiency data, EPA has concluded that smokeless flares designed for and operated under certain conditions are acceptable alternatives to enclosed combustion devices (incinerators, boilers, process heaters) or vapor recovery systems, such as carbon adsorbers and condensation units. For example, steam-assisted flares must have flare gas heat contents greater than 11.2 megajoules per standard cubic meter and exit velocities less than 18 meters per second. Flares achieving these conditions are acceptable because they achieve more than 95 percent emission reduction. The presence of a flame can be ensured by monitoring the flare's pilot light with an appropriate heat sensor, such as a thermocouple. To ensure smokeless operation, visible emissions from a flare would be limited to less than 5 minutes in any 2-hour period as determined by Reference Method 22.

Import on Small Manufacturers

Comment: Commenters requested an exemption for small manufacturers. These commenters were mostly concerned with the impact on process units with few equipment and process units with low production volumes.

Respone: Data from test work on equipment leaks of VOC, however, do not show any definite relationship between emissions and production volume. Equipment leaks of VOC and the cost of their control are proportional to the number of equipment components in a plant rather than the plant size or production volume. However, there are some process units (e.g., research and development facilities) which have production rates so small that their VOC emissions from equipment leaks are likely to be very small and, as a consequence, the cost to control these emissions would be unreasonably high. EPA has excluded from the standards process units producing less than 1,000 Mg/yr. The lower production rate cutoff was developed on the basis of cost and emission reduction considerations and is explained in Section 5.7 of the BID for the promulgated standards.

Test Method and Monitoring

Comment: Commenters requested that hexane be the required calibration gas for the application of Reference Method 21 to SOCMI leak detection and repair programs. Reference Method 21 specifies the monitor and the methodology to be used to detect leaks for required leak detection and repair programs. The proposed standards required that methane be used as the calibration gas. Two reasons were given for their desire to use hexane. First, commenters believed (on the basis of response factors) that the use of methane would result in the detection of more leaks. Second, there is at least one type of portable VOC detector which responds to hexane but does not respond to methane.

Response: EPA considered the differences between leak frequencies found using hexane and leak frequencies found using methane. The differences are not significant. The variability seen in repeat sampling of the same piece of equipment was 23 percent. The variability is in the same range as the 30 percent difference seen in response between the TLV-hexane system and the OVA-methane systems at the 10,000 ppmv definition of a leak. Because the variability in repeat sampling is similar to the differences in response at 10,000 ppmv, the data can be used interchangeably within 30 percent at the action level. Because an error of 30 percent at the action level is a small error considering all the errors associated with leak detection, there is no need to change the required calibration gas on the basis offered by the commenters. However, since some types of analyzers may be useful in certain SOCMI process units, and these types do not respond to methane, hexane has been added to the regulation as an alternate calibration material.

The use of hexane as an alternate calibration material is not limited to a single type of detector. The owner or operator may choose to use either calibrant with any allowable instrument. However, in any performance test conducted by EPA or a State agency, the VOC detector is likely to be calibrated with methane, even if the calibrant selected by the owner or operator is different, because methane calibrants are easier to obtain and deteriorate less than hexane calibrants.

Docket

The docket is an organized and complete file of all the information considered by EPA in the development of this rulemaking.The docket is a dynamic file, since material is added throughout the rulemaking process. The docketing system is intended to allow members of the public and industries involved to identify and locate documents so that they can participate effectively in the rulemaking process. Along with the statement of basis and purpose of the proposed and promulgated standards and EPA responses to significant commets, the contents of the docket will serve as the record in case of judicial review, except for interagency review materials [Section 307(d)(7)(A)].

Miscellaneous

In accordance with Section 117 of the Act, publication of these promulgated standards was preceded by consultation with appropriate advisory committees, independent experts, and Federal departments and agencies. This regulation will be reviewed 4 years from the date of promulgation as required by the Clean Air Act. This review will include an assessment of such factors as the need for integration with other programs, the existence of alternative methods, enforceability, improvements in emission control technology, and reporting requirements.

Section 317 of the Clean Air Act requires the Administrator to prepare an economic impact assessment for any new source standard of performance promulgated under Section 111(b) of the Act. An economic impact assessment was prepared for this regulation and for other regulatory alternatives. All aspects of the assessment were considered in the formulation of the standards to insure that cost was carefully considered in determining the best demonstrated technology. The economic impact assessment is included in the background information documents for the proposed standards and the promulgated standards.

Information collection requirements associated with this regulation (those included in 40 CFR Part 60, Subpart A and Subpart VV) have been approved by the Office of Management and Budget (OMB) under the provisions of the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.* and have been assigned OMB control number 2060-0012.

"Major Rule" Determination. Under Executive Order 12291, the Administrator is required to judge whether a regulation is a "major rule" and, therefore, subject to certain requirements of the Order. The Administrator has determined that this regulation would result in none of the adverse economic effects set forth in Section 1 of the Order as grounds for finding a regulation to be a "major rule." Fifth-year annualized costs of the standards would be as much as $3.3 million for the 830 newly constructed, modified, and reconstructed production facilities projected that could be affected by the standards during the first 5 years. Significant price increases are not expected to result from

implementation of these standards because the annualized cost is a small fraction (about 0.25 percent) of the yearly revenue expected for the new, modified, and reconstructed units affected during the 5-year period. The Administrator has concluded that this rule is not "major" under any of the criteria established in the Executive Order.

As discussed in the "Basis For The Final Standards" section of this preamble, costs per megagram of VOC emission reduction were used in selecting the standards promulgated by this rulemaking. This regulation was submitted to the OMB for review as required by Executive Order 12291. Any comments from OMB to EPA and any EPA responses to those comments are available for public inspection in Docket No. A-79-32, Central Docket Section, at the address given in the ADDRESSES section of this preamble.

Regulatory Flexibility Analysis Certification. The Regulatory Flexibility Act of 1980 requires that adverse effects of all Federal regulations upon small businesses be identified. According to current Small Business Administration guidelines, a small business in the organic chemical manufacturing industry is one that has 1,000 employees or fewer. Current estimates indicate between 10 and 30 percent of the existing industry employ fewer than 1,000 people. Even if facilities owned by small businesses do become subject to the standards, none will be adversely affected. This conclusion is based on the finding that the annualized cost of the standards would be less than 0.25 percent of the yearly revenue expected for units affected by the standards. This finding reflects the economic impact for facilities owned by small businesses and is not considered significant. Pursuant to the provisions of 5 U.S.C. 605(b), I hereby certify that this rule will not have a significant economic impact on a substantial number of small entities.

List of Subjects in 40 CFR Part 60

Air pollution control, Aluminum, Ammonium sulfate plants, Asphalt, Cement industry, Coal Copper, Electric power plants, Glass and glass products, Grains, Intergovernmental relations, Iron, Lead, Metals, Metallic Minerals, Motor vehicles, Nitric acid plants, Paper and paper products industry, Petroleum, Phosphate, Sewage disposal, Steel Sulfuric acid plants, Waste treatment and disposal, Zinc, Tires, Incorporation by Reference, Can surface coating, Sulfuric acid plants, Industrial organic chemicals.

Dated: September 30, 1983.

William D. Ruckelshaus,
Administrator.

PART 60—[AMENDED]

40 CFR Part 60 is amended as follows:

1. By adding paragraph (f) to § 60.7 of Subpart A—General Provisions as follows:

§ 60.7 Notification and recordkeeping.

* * * * *

(f) Individual subparts of this part may include specific provisions which clarify or make inapplicable the provisions set forth in this section.

(Sec. 111, 114, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411) 7601(a)))

2. By adding paragraph (f) to § 60.11 of Subpart A—General Provisions as follows:

§ 60.11 Compliance with standards and maintenance requirements.

* * * * *

(f) Special provisions set forth under an applicable subpart of this part shall supersede any conflicting provisions of this section.

(Sec. 111, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7601(a)))

3. By adding paragraphs (a)(34), (a)(35), (a)(36), (a)(37), (a)(38), and (a)(39) to § 60.17 of Subpart A—General Provisions as follows:

§ 60.17 Incorporations by reference.

* * * * *

(a)

(34) ASTM. E169-63 (Reapproved 1977), General Techniques of Ultraviolet Quantitative Analysis, IBR approved for § 60.485(d).

(35) ASTM E168-67 (Reapproved 1977), General Techniques of Infrared Quantitative Analysis, IBR approved for § 60.485(d).

(36) ASTM E260-73, General Gas Chromatography Procedures, IBR approved for § 60.485(d).

(37) ASTM D2879-70, Vapor Pressure—Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope, IBR approved for § 60.485(e).

(38) ASTM D2382-76, Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method), IBR approved for § 60.485(g).

(39) ASTM D2504-67 (Reapproved 1977), Noncondensable Gases in C_2 and Lighter Hydrocarbon Products by Gas Chromatography, IBR approved for § 60.485(g).

(Sec. 111, 114, 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411) 7601(a))).

4. By adding a new Subpart VV as follows:

Subpart VV—Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry

Sec.
60.480 Applicability and designation of affected facility.
60.481 Definitions.
60.482-1 Standards: General.
60.482-2 Standards: Pumps in light liquid service.
60.482-3 Standards: Compressors.
60.482-4 Standards: Pressure relief devices in gas/vapor service.
60.482-5 Standards: Sampling connection systems.
60.482-6 Standards: Open-ended valves or lines.
60.482-7 Standards: Valves in gas/vapor and in light liquid service.
60.482-8 Standards: Pumps and valves in heavy liquid service, pressure relief devices in light liquid or heavy liquid service, and flanges and other connectors.
60.482-9 Standards: Delay of repair.
60.482-10 Standards: Closed vent systems and control devices.
60.483-1 Alternative standards for valves—allowable percentage of valves leaking.
60.483-2 Alternative standards for valves—skip period leak detection and repair.
60.484 Equivalence of means of emission limitation.
60.485 Test methods and procedures.
60.486 Recordkeeping requirements.
60.487 Reporting requirements.
60.488 [Reserved]
60.489 List of chemicals produced by affected facilities.

Authority: Sec. 111 and 301(a) of the Clean Air Act, as amended (42 U.S.C. 7411, 7601(a)), and additional authority as noted below.

Subpart VV—Standards of Performance for Equipment Leaks of VOC in the Synthetic Organic Chemicals Manufacturing Industry

§ 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 of one of the exemptions in this paragraph, then the owner or operator shall maintain records as required in § 60.486(h).

(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.

"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.

"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.

"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)(4).

§ 60.482-2 StandardsD 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 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 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).

§ 50.482-3 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.

§ 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 lead 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 § 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 becomes an affected facility through § 60.14 or § 60.15, 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.

§ 60.482-8 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 required in § 60.482-7(d)(1),

(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 desclibed in § 60.482-3(f),

(vi) Number of compressors for which leaks were not reported as required in § 60.482-3(g)(1); and

(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 [Reserved]

§ 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.
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.

CAS No. *	Chemical
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, 535-80-6, 74-11-3 *.	Chlorobenzoic acid.
2136-81-4, 2136-89-2, 5216-25-1 *.	Chlorobenzotrichloride.
1321-03-5	Chlorbenzoyl chloride.
25497-29-4	Chlorodifluoromethane.
75-45-6	Chlorodifluoroethane.
67-66-3	Chloroform.
25586-43-0	Chloronepthalene.
88-73-3	o-chloronitrobenzone.
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.
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, 626-43-7, 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	Dioxilane.
122-39-4	Diphenylamine.
101-84-8	Diphenyl oxide.
102-08-9	Diphenyl thiourea.
25265-71-8	Dipropylene glycol.
25378-22-7	Dodecene.
28675-17-4	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	Ethyine 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 monoethy ether.
111-15-9	Ethylene glycol monethyl 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.
95-92-1	Ethyl oxalate.
41892-71-1	Ethyl sodium oxalacetate.
50-00-0	Formaldehyde.
75-12-7	Formamide.
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.
124-00-4	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.
141-79-7	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.
37365-71-2	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.
75-98-9	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.
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, 25036-29-7 *.	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.

CAS No. [a]	Chemical
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 [c]	Toluenesulfonic acids.
98-59-9	Toluenesulfonyl chloride.
26915-12-8	Toluidines.
87-61-6, 108-70-3, 120-82-1 [c].	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.

[a] 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.

[b] No CAS number(s) have been assigned to this chemical, its isomers, or mixtures containing these chemicals.

[c] 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.

5. In Appendix A of Part 60, Method 18 is added as follows:

Method 18—Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

Introduction

(This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.)

1. *Applicability and Principle*

1.1 Applicability. This method applies to the analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources.

This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.2 Principle. This method is based on separating the major components of a gas mixture with a gas chromatograph (GC) and measuring the separated components with a suitable detector.

The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

2. *Range and Sensitivity*

2.1 Range. The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

3. *Precision and Accuracy*

Gas chromatographic techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Duplicate analyses are within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

4. *Interferences*

Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately, is best dealt with by thorough purging of the GC sample loop between samples.

To assure consistent detector response, calibration gases are contained in dry air. To eliminate errors in concentration calculations due to the volume of water vapor in the samples, moisture concentrations are determined for each sample, and a correction factor is applied to any sample with greater than 2 percent water vapor.

5. *Presurvey and Presurvey Sampling*

A presurvey shall be performed on each source to be tested. The purpose of the presurvey is to obtain all information necessary to design the emission test. The most important presurvey data are the average stack temperature and temperature range, approximate particulate concentration, static pressure, water vapor content, and identity and expected concentration of each organic compound to be analyzed. Some of this information can be obtained from literature surveys, direct knowledge, or plant personnel. However, presurvey samples of the gas shall be obtained for analysis to confirm the identity and approximate concentrations of the specific compounds prior to the final testing.

5.2 Apparatus.

5.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

5.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

5.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

5.1.4 Flow Meter. To accurately monitor sample loop flow rate of 100 ml/min.

5.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

5.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

5.1.7 Syringes. 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing standards and for injecting head space vapor from liquid standards in retention time studies.

5.1.8 Tubing Fittings. To plumb GC and gas cylinders.

5.1.9 Septums. For syringe injections.

5.1.10 Glass Jars. If necessary, clean-colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

5.1.11 Soap Film Flow Meter. To determine flow rates.

5.1.12 Tedlar Bags. 10- and 50-liter capacity, for preparation of standards.

5.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ±2 percent, for perparation of gas standards.

5.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

5.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

5.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD-2, etc.) for presurvey samples.

5.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

5.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

5.2 Reagents.

5.2.1 Deionized Distilled Water.

5.2.2 Methylene Dichloride.

5.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

5.2.4 Calibration Solutions. Samples of all the compounds of interest in a liquid form, for retention time studies.

5.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

5.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

5.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatability with the column.

5.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

5.3 Sampling.

5.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples can be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene dichloride. Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace and apply heat up to 500° C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Grease the stopcocks with stopcock grease and return them to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape.

Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

5.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

5.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in Section 5.3.1.1. Place the filter end of the probe at the centroid of the duct, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

5.3.2 Flexible Bag Procedure. Tedlar or aluminized Mylar bags can also be used to obtain the presurvey sample. Use new bags, and leak check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak check and sample collection procedures given in Section 7.1.

5.3.3 Determination of Moisture Content. For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 59° C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

5.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

5.5 Collection of Presurvey Samples with Adsorption Tube. Follo Section 7.4 for presurvey sampling.

6. *Analysis Development*

Presurvey samples shall be used to develop and confirm the best sampling and analysis scheme.

6.1 Selection of GC Parameters.

6.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search, contact with manufacturers of GC columns, and discussion with personnel at the emission source.

Most column manufacturers keep excellent records of their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations.

Plants with analytical laboratories may be able to provide information on their analytical procedures, including extractions, detector type, column types, compounds emitted, and approximate concentrations.

6.1.2 Preliminary GC Adjustment. Using the standards and column obtained in Section 6.1.1, perform initial tests to dertermine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

6.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

6.1.4 Presurvey Sample Analysis. Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

Use the GC conditions determined by the procedures of Section 6.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 6.3) to obtain an estimate of the concentrations.

Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

6.2 Calibration Standards. If the presurvey samples are collected in an adsorbent tube (charcoal, XAD-2, Tenax, etc.), prepare the standards in the same solvent used for the extraction procedure for the adsorbent. Prepare several standards for each compound throughout the range of the sample.

6.2.1 Cylinder Calibration Gases. If available, use NBS reference gases or commercial gas mixtures certified through direct analysis for the calibration curves.

6.2.1.1 Optional Cylinder Approach. As an alternative procedure, maintain high and low calibration standards. Use the high concentration (50 to 100 ppm) standard to prepare a three-point calibration curve with an appropriate dilution technique. Use this same approach also to verify the dilution techniques for high-concentration source gases.

To prepare the diluted calibration samples, use calibrated rotameters to meter both the high concentration calibration gas and the diluent gas. Adjust the flow rates through the rotameters with micrometer valves to obtain the desired dilutions. A positive displacement pump or other metering techniques may be used in place of the rotameter to provide a fixed flow of high concentration gas.

To calibrate the rotameters, connect each rotameter between the diluent gas supply and a suitably sized bubble meter, spirometer, or wet test meter. While it is desirable to calibrate the calibration gas flowmeter with calibration gas, generally the available amount of this gas will preclude it. The error introduced by using the diluent gas is insignificant for gas mixtures of up to 1,000 to 2,000 ppm of each organic component. Record the temperature and atmospheric pressures as follows:

$$Q_2 = Q_1\left(\frac{P_2T_1}{P_1\,T_2}\right)^{1/2} \quad \text{Eq. 18-1}$$

Where:

Q_2 = Flow rate at new absolute temperature (T_2) and new absolute pressure (P_2).

Q_1 = Flow rate at calibration absolute temperature (T_1) and absolute pressure (P_1).

Connect the rotameters to the calibration and diluent gas supplies using 6-mm Teflon tubing. Connect the outlet side of the rotameters through a connector to a leak-free Tedlar bag as shown in Figure 18.5. (See Section 7.1 for leak check procedures.) Adjust the gas flows to provide the desired dilution, and fill the bag with sufficient gas for calibration. Be careful not to fill to the point where it applies additional pressure on the gas. Record the flow rates of both rotameters, the ambient temperature, and atmospheric pressure. Calculate the concentration of diluted gas as follows:

$$C_a = \frac{10^6(\overline{X}_a\, q_a)}{q_a + q_d} \quad \text{Eq. 18-2}$$

Where:

C_a = Concentration of component "a" in ppm.

$\overline{X}_a$ = Mole fraction of component "a" in the calibration gas to be diluted.

q_a = Flow rate of the calibration gas contains mg component "a" at measured temperature and pressure.

q_d = Diluent gas flow at measured temperature and pressure.

Use single-stage dilutions to prepare calibration mixtures up to about 1:20 dilution factor. For greater dilutions, use a double dilution system. Assemble the apparatus, as shown in Figure 18-6, using calibrated flowmeters of suitable range. Adjust the control valves so that about 90 percent of the diluted gas from the first stage is exhausted, and 10 percent goes to the second stage flowmeter. Fill the Tedlar bag with the dilute gas from the second stage. Record the temperature, ambient pressure, and water manometer pressure readings. Correct the flow reading in the first stage as indicated by the water manometer reading. Calculate the concentration of the component in the final gas mixture as follows:

$$C_a = 10^6\,\overline{X}_a\left(\frac{q_a1}{q_a1 + q_d1}\right)\left(\frac{q_a2}{q_a2 + q_d2}\right) \quad \text{Eq. 18-3}$$

Where:

C_a = Concentration of component "a" in ppm.

$\overline{X}_a$ = Mole fraction of component "a" in original gas.

q_a1 = Flow rate of component "a" in stage 1.

q_a2 = Flow rate of component "a" in stage 2.

q_d1 = Flow rate of diluent gas in stage 1.

q_d2 = Flow rate of diluent gas in stage 2.

Further details of the calibration methods for rotameters and the dilution system can be found in Citation 21 in Section 8.

6.2.2 Preparation of Standards from Volatile Materials. Record all data shown on Figure 18-3.

6.2.2.1 Bag Technique. Evacuate a 10-liter Tedlar bag that has passed a leak check (see Section 7.1), and meter in 5.0 liters of nitrogen through a 0.5 liter per revolution dry test meter. While the bag is filling, use a 0.5-ml syringe to inject a known quantity of the material of interest through the wall of the bag or through a septum—caped tee at the bag inlet. Withdraw the syringe needle, and immediately cover the resulting hole with a piece of masking tape. In a like manner, prepare dilutions having other concentrations. Prepare a minimum of three concentrations. Place each bag on a smooth surface, and alternately depress opposite sides of the bag 50 times to mix the gases. Record the average meter temperature, gas volume, liquid volume, barometric pressure, and meter pressure.

Set the electrometer attenuator to the X1 Position. Flush the sampling loop with zero helium or nitrogen, and activate the sample valve. Record the injection time, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record peaks and detector responses that occur in the absence of any sample. Maintain conditions. Flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the calibration mixtures, and open the sample valve. Record the injection time. Select the peak that corresponds to the compound of interest. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. Divide this quantity by the chart speed, and record the resulting value as the retention time.

6.2.2.2 Preparation of Standards from less Volatile Liquid Materials. Use the equipment shown in Figure 18-8. Calibrate the dry gas meter with a wet test meter or a spirometer. Use a water manometer for the pressure gauge and glass, Teflon, brass, or stainless steel for all connections. Connect a valve to the inlet of the 50-liter Tedlar bag.

To prepare the standards, assemble the equipment as shown in Figure 18-8, and leak check the system. Completely evacuate the bag. Fill the bag with hydrocarbon-free air, and evacuate the bag again. Close the inlet valve.

Turn on the hot plate, and allow the water to reach boiling. Connect the bag to the impinger outlet. Record the initial meter reading, open the bag inlet valve, and open the cylinder. Adjust the rate so that the bag will be completely filled in approximately 15 minutes. Record meter pressure, temperature, and local barometric pressure.

Fill the syringe to the desired liquid volume with the material to be evaluated. Place the syringe needle into the impinger inlet using the septum provided, and inject the liquid into the flowing air stream. Use a needle of sufficient length to permit injection of the liquid below the air inlet branch of the tee. Remove the syringe.

Complete filling of the bag; note and record the meter pressure and temperature at regular intervals, preferably 1 minute.

When the bag is filled, stop the pump, and close the bag inlet valve. Record the final meter reading.

Disconnect the bag from the impinger outlet, and set it aside for at least 1 hour to equilibrate. Analyze the sample within the proven life period of its preparation.

6.2.2.3 Concentration Calculations. Average the meter temperature (T_m) and pressure (P_m) readings over the bag filling process.

Measure the solvent liquid density at room temperature by accurately weighing a known volume of the material on an analytical balance to the nearest 1.0 milligram. Take care during the weighing to minimize evaporation of the material. A ground-glass stoppered 25-ml volumetric flask or a glass-stoppered specific gravity bottle is suitable for weighing. Calculate the result in terms of g/ml. As an alternative, literature values of the density of the liquid at 20°C may be used.

Calculate the concentration of material in the sample in mg/liter at standard conditions as follows:

$$C_{std\ sol} = \frac{760(L_v)(p)(273 + T_m)}{273(M_f - M_i)(P_{bar} + P_m)} \quad \text{Eq. 18-4}$$

Where:

$C_{std\ sol}$ = Standard solvent concentration, mg/std liter.

L_v = Liquid volume injected, ml.

p = Liquid density at room temperature, g/ml.

T_m = Meter temperature, °C.

M_f,M_i = Final and initial meter reading, liters.

P_{bar} = Local barometric pressure (absolute), mm Hg.

P_m = Meter pressure (gauge), mm Hg.

6.3 Preparation of Calibration Curves. Obtain gas standards as described in Section 6.2 such that three concentrations per attentuator range are available. Establish proper GC conditioning, then flush the sampling loop for 30 seconds at a rate of 100 ml/min. Allow the sample loop pressure to equilibrate with atmospheric pressure, and activate the injection valve. Record the standard concentration, attentuator setting, injection time, chart speed, retention time, peak area, sample loop, temperature, column temperature, and carrier gas flow rate. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their average. The average multiplied by the attenuator setting is then the calibration area value for that concentration.

Repeat this procedure for each standard. Plot concentrations along the abscissa and the calibration area values along the ordinate. Perform a regression analysis, and draw the least squares line.

6.4 Optional Use of Prepared Cylinders for Dilution Calibration Checks, and Response Factor Determinations. A set of three standards of the major component in the emissions is required. This set of standards can be taken into the field and thereby replace the need to prepare standards as described in Section 6.2.2.

The high concentration standard can be run through the dilution system to assess the accuracy of the system. First, prepare a calibration curve using the three standards following the procedure described in Section 6.3. Then, prepare a dilute sample using the high concentration standard so that the dilute sample will fall within the lower limits of the calibration curve.

Next, analyze the dilute sample, and calculate the measured concentration from the calibration curve as described in Section 6.3. The dilute concentration calculated from the analysis shall be within 10 percent of the concentration expected from the dilution system; otherwise determine the source of error in the dilution system, and correct it.

The calibration curve from the cylinder standards for a single organic can also be related to the GC response curves of all the compounds in the source by response factors developed in the laboratory. In the field, the single calibration curve from the cylinder standards and the calculated response factors measured in the laboratory can then be used to replace the need to prepare and analyze calibration standards for each organic compound (see Section 6.5 on daily quality control procedure).

Recheck the relative peak area of one of the calibration standards daily to guard against degradation. If the relative peak areas on successive days differ by more than 5 percent, remake all of the standards before proceeding to the final sample analyses.

6.5 Evaluation of Calibration and Analysis Procedure. Immediately after the preparation of the calibration curve and prior to the final sample analyses, perform the analysis audit described in Part 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis" (47 FR 39179, September 7, 1982). The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 18–3 and 18–7. The audit analyses shall agree with the audit concentrations within 10 percent. When available, the tester may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided: (a) the gas manufacturer certifies the audit cylinder as described in Section 5.2.3.1 of Method 23 and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined as an analysis performed by an individual other than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

7. Final Sampling and Analysis Procedure

Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 7.1, 7.2, 7.3, or 7.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique. If the source temperature is below 100°C, and the organic concentrations are suitable for the detector to be used, use the direct interface method. If the source gases require dilution, use a dilution interface and either the bag sample or adsorption tubes. The choice between these two techniques will depend on the physical layout of the site, the source temperature, and the storage stability of the compounds if collected in the bag. Sample polar compounds by direct interfacing or dilution interfacing to prevent sample loss by adsorption on the bag.

7.1 Integrated Bag Sampling and Analysis

7.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Therefore, check both the bags and the container for leaks before and after use as follows: Connect a water manometer using a tee connector between the bag or rigid container and a pressure source. Pressurize the bag or container to 5 to 10 cm H_2O (2 to 4 in. H_2O), and allow it to stand overnight. A deflated bag indicates a leak.

7.1.1.1 Apparatus.

7.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with 6.4-mm OD Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

7.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

7.1.1.1.3 Needle Valve. To control gas flow.

7.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

7.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

7.1.1.1.6 Flowmeter. 0 to 500-ml flow range; with manufacturer's calibration curve.

7.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18–9. Leak check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack, and start the pump with the needle valve adjusted to yield a flow of 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18–10. Protect the Tedlar bag and its container from sunlight. When possible, perform the analysis within 2 hours of sample collection.

7.1.2 Direct Pump Sampling Procedure. Flow 7.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of stainless steel or some other material not affected by the stack gas. Leak check the system, and then purge with stack gas before the connecting to the previously evacuated bag.

7.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 7.1.1 except replace the pump with another evacuated can (see Figure 18–9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

7.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection, and maintain it at a suitably elevated temperature during all subsequent operations. (Note: Take care to leak check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the Tedlar bag.

In the first procedure, heat the box containing the sample bag to the source temperature, provided the components of the bag and the surrounding box can withstand this temperature. Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to source temperature until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

To use the second procedure, prefill the Tedlar bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 6.2.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or

Teflon positive displacement pump. Verify the dilution factors periodically through dilution and analysis of gases of known concentration.

7.1.5 Analysis of Bag Samples. Connect the needle valve, pump, charcoal tube, and flowmeter to draw gas samples through the gas sampling valve. Flush the sample loop with gas from one of the three Tedlar bags containing a calibration mixture, and analyze the sample. Obtain at least two chromatograms for the sample. The results are acceptable when the peak areas from two consecutive injections agree to within 5 percent of their average. If they do not agree, run additional samples until consistent area data are obtained. If this agreement is not obtained, correct the instrument technique problems before proceeding. If the results are acceptable, analyze the other two calibration gas mixtures in the same manner. Prepare the calibration curve by using the least squares method.

Analyze the two field audit samples as described in Section 6.5 by connecting each Tedlar bag containing an audit gas mixture to the sampling valve. Calculate the results; record and report the data to the audit supervisor. If the results are acceptable, proceed with the analysis of the source samples.

Analyze the source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Follow the restrictions on replicate samples specified for the calibration gases. Record the data. Analyze the other two bag samples of source gas in the same manner. After all three bag samples have been analyzed, repeat the analysis of the calibration gas mixtures. Use the average of the two calibration curves to determine the respective sample concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by both calibration curves.

7.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

Use the field analytical data sheet as shown in Figure 18–11. The sheet has been designed to tabulate information from the bag collection, direct interface, and dilution interface systems; as a result, not all of the requested information will apply to any single method. Note the data that do not apply with the notation "N.A." Summarize the analysis.

7.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. Adhere to all safety requirements with this method.

7.2.1 Apparatus.

7.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as required by duct temperature, 6.4-mm OD, enlarged at duct end to contain glass wool plug. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining duct temperature.

7.2.1.2 Sample Lines. 6.4-mm OD Teflon lines, heat-traced to prevent condensation of material.

7.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

7.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

7.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

7.2.1.6 Needle Valve. To control gas sampling rate from the source.

7.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

7.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

7.2.1.9 Charcoal Adsorber. To adsorb organic vapor collected from the source to prevent exposure of personnel to source gas.

7.2.1.10 Gas Cylinders. Carrier gas (helium or nitrogen), and oxygen and hydrogen for a flame ionization detector (FID) if one is used.

7.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

7.2.1.12 Recorder/Integrator. To record results.

7.2.2 Procedure. To obtain a sample, assemble the sampling system as shown in Figure 18–12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the source temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature of 0 to 3°C above the source temperature. While the probe and heated line are being heated, disconnect the sample line from the gas sampling valve, and attach the line from the calibration gas mixture. Flush the sample loop with calibration gas and analyze a portion of that gas. Record the results. After the calibration gas sample has been flushed into the GC instrument, turn the gas sampling valve to flush position, then reconnect the probe sample line to the valve. Move the probe to the sampling position, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the sample using the same conditions as for the calibration gas mixture. Repeat the analysis on an additional sample. Measure the peak areas for the two samples, and if they do not agree to within 5 percent of their mean value, analyze additional samples until two consecutive analyses meet this criteria. Record the data. After consistent results are obtained, remove the probe from the source and analyze a second calibration gas mixture. Record this calibration data and the other required data on the data sheet shown in Figure 18–11, deleting the dilution gas information.

(Note.—Take care to draw all samples, calibration mixtures, and audits through the sample loop at the same pressure.)

In addition, analyze the field audit samples by connecting the audit sample cylinders to the gas sampling valve. Use the same instrument conditions as were used for the source samples. Record the data, and report the results of these analyses to the audit supervisor.

7.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the Section 7.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

7.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

7.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120°C and deliver 1.5 liters/minute.

7.3.1.2 Dilution Pumps. Two Model A–150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

7.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to 6.4-mm OD Teflon tubing.

7.3.1.4 Flowmeters. Two, for measurement of diluent gas, expected delivery flow rate to be 1,350 cc/min.

7.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

7.3.1.6 Heated Box. Suitable for being heated to 120°C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) The heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18–13.

(Note.—Care must be taken to leak check the system prior to the dilutions so as not to create a potentially explosive atmosphere.)

The heated box shown in Figure 18–13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box.

In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

7.3.2 Procedure. Assemble the apparatus by connecting the heated box, shown in Figure 18–13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct. Measure the source temperature, and adjust all heating units to a temperature 0 to 3°C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds. Verify the operation of the dilution system by analyzing a high concentration gas of known composition through either the 10:1 or 100:1 dilution stages, as appropriate. (If necessary, vary the flow of the diluent gas to obtain other dilution ratios.) Determine the concentration of the diluted calibration gas using the dilution factor and the calibration curves prepared in the laboratory. Record the pertinent data on the data sheet shown in Figure 18–11. If the data on the diluted calibration gas are not within 10 percent of the expected values, determine whether the chromatograph or the dilution system is in error, and correct it. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop, bypassing the dilution system. If these analyses are not within acceptable limits, correct the dilution system to provide the desired dilution factors. Make this correction by diluting a high-concentration standard gas mixture to adjust the dilution ratio as required.

Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards. Repeat the analyses until two consecutive values do not vary by more than 5 percent from their mean value are obtained.

Repeat the analysis of the calibration gas mixtures to verify equipment operation. Analyze the two field audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

7.4 Adsorption Tube Procedure (Alternative Procedure). It is suggested that the tester refer to the National Institute of Occupational Safety and Health (NIOSH) method for the particular organics to be sampled. The principal interferent will be water vapor. If water vapor is present at concentrations above 3 percent, silica gel should be used in front of the charcoal. Where more than one compound is present in the emissions, then develop relative adsorptive capacity information.

7.4.1 Additional Apparatus. In addition to the equipment listed in the NIOSH method for the particular organic(s) to be sampled, the following items (or equivalent) are suggested.

7.4.1.1 Probe (Optional). Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-stack heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

7.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

7.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices to provide pumping rates from approximately 10 to 100 cc/min.

7.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within ± 1 percent, to calibrate pump.

7.4.1.5 Stopwatch. To time sampling and pump rate calibration.

7.4.1.6 Adsorption Tubes. Similar to ones specified by NIOSH, except the amounts of adsorbent per primary/backup sections are 800/200 mg for charcoal tubes and 1040/260 mg for silica gel tubes. As an alternative, the tubes may contain a porous polymer adsorbent such as Tenax GC or XAD–2.

7.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

7.4.1.8 Rotameter. 0 to 100 cc/min, to detect changes in flow rate during sampling.

7.4.2 Sampling and Analysis. It is suggested that the tester follow the sampling and analysis portion of the respective NIOSH method section entitled "Procedure." Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

Use a sample probe, if required. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. When more than one organic is present in the emissions, then develop relative adsorptive capacity information. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacture's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Analyze the audit samples (see Section 7.4.4.3), then the emission samples. Repeat the analysis of each sample until the relative deviation of two consecutive injections does not exceed 5 percent.

7.4.3 Standards and Calibration. The standards can be prepared according to the respective NIOSH method. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses. Prepare the calibration curve by using the least squares method.

7.4.4 Quality Assurance.

7.4.4.1 Determination of Desorption Efficiency. During the testing program, determine the desorption efficiency in the expected sample concentration range for each batch of adsorption media to be used. Use an internal standard. A minimum desorption efficiency of 50 percent shall be obtained. Repeat the desorption determination until the relative deviation of two consecutive determinations does not exceed 5 percent. Use the average desorption efficiency of these two consecutive determinations for the correction specified in Section 7.4.4.5. If the desorption efficiency of the compound(s) of interest is questionable under actual sampling conditions, use of the Method of Standard Additions may be helpful to determine this value.

7.4.4.2 Determination of Sample Collection Efficiency. For the source samples, analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and backup), repeat the sampling with a larger sampling portion.

7.4.4.3 Analysis Audit. Immediately before the sample analyses, analyze the two audits in accordance with Section 7.4.2. The analysis audit shall agree with the audit concentration with 10 percent.

7.4.4.4 Pump Leak Checks and Volume Flow Rate Checks. Perform both of these checks immediately after sampling with all sampling train components in place. Perform all leak checks according to the manufacturer's instructions, and record the results. Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

7.4.4.5 Calculations. All calculations can be performed according to the respective NIOSH method. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results by dividing by the desorption efficiency (decimal value). Report results as ppm by volume, dry basis.

7.5 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data sheets shown in Figure 18–11 have been completed. Summarize this data on the data sheets shown in Figure 18–15.

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BILLING CODE 6560-50-M

I. Name of company ______________ Date ________

Address ______________

____

Contacts ______________ Phone ________

______________ ________

Process to be sampled ______________

____

____

Duct or vent to be sampled ______________

____

II. Process description ______________

____

____

____

____

Raw material ______________

____

______________ ______________

Products ______________

____

____

Operating cycle

Check: Batch ______ Continuous ______ Cyclic ______

Timing of batch or cycle ______________

Best time to test ______________

Figure 18-1. Preliminary survey data sheet.

III. Sampling site

A. Description

Site description ______________

Duct shape and size ______________

Material ______________

Wall thickness ______________ inches

Upstream distance ________ inches ________ diameter

Downstream distance ________ inches ________ diameter

Size of port ______________

Size of access area ______________

Hazards ______________ Ambient temp. ______ °F

B. Properties of gas stream

Temperature _____ °C _____ °F, Data source ________

Velocity ______________, Data source ________

Static pressure ___ inches H_2O, Data source ________

Moisture content ________ %, Data source ________

Particulate content ________, Data source ________

Gaseous components

N_2 ________ % Hydrocarbons ______ ppm

O_2 ________ % ________ ______

CO ________ % ________ ______

CO_2 ________ % ________ ______

SO_2 ________ % ________ ______

Hydrocarbon components

________ ______ ppm

________ ______ ppm

________ ______ ppm

________ ______ ppm

________ ______ ppm

________ ______ ppm

Figure 18-1 (continued). Preliminary survey data sheet.

C. Sampling considerations

Location to set up GC ____________________

____

Special hazards to be considered ____________________

____

Power available at duct ____________________

Power available for GC ____________________

Plant safety requirements ____________________

____

Vehicle traffic rules ____________________

____

Plant entry requirements ____________________

____

Security agreements ____________________

____

Potential problems ____________________

____

D. Site diagrams. (Attach additional sheets if required).

Figure 18-1 (continued). Preliminary survey data sheet.

Components to be analyzed	Expected concentration

Suggested chromatographic column ____________________

____

Column flow rate ____ml/min   Head pressure____ mm Hg

Column temperature:

Isothermal __________°C

Programmed from _____°C to ____°C at ____°C/min

Injection port/sample loop temperature ______°C

Detector temperature _______°C

Detector flow rates: Hydrogen _____ml/min.

head pressure____ mm Hg

Air/Oxygen _____ml/min,

head pressure____ mm Hg

Chart speed __________ inches/minute

Compound data:

Compound	Retention time	Attenuation

Figure 18-2. Chromatographic conditions data sheet.

Calibration Curve Data - Volatile and Liquid Samples Collected in a Tedlar Bag

	Blank	Mixture 1	Mixture 2	Mixture 3
Size of Tedlar bag (liters)	____	____	____	____
Dilution gas (name)	____	____	____	____
Vol. of dilution gas (liters)		____	____	____
Component (name)		____	____	____
Volume of component (ml)		____	____	____
Average meter temp. (°C)		____	____	____
Average meter pressure (mm)		____	____	____
Atmospheric pressure (mm)		____	____	____
Density of liquid component (g/ml)		____	____	____
Sample loop volume (ml)	____	____	____	____
Sample loop temp. (°C)	____	____	____	____
Carrier gas flow rate (ml/min)	____	____	____	____
Column temperature				
initial (°C)	____	____	____	____
program rate (°C/min)	____	____	____	____
final (°C)	____	____	____	____
Injection time (24 hr. basis)	____	____	____	____
Distance to peak (cm)	____	____	____	____
Chart speed (cm/min)	____	____	____	____
Retention time (min)	____	____	____	____
Calculated concentration (ppm)	____	____	____	____
Attenuator setting	____	____	____	____
Peak height (mm)	____	____	____	____
Peak area (mm^2)	____	____	____	____
Area x attenuation	____	____	____	____

Plot peak area x attenuation against concentration to obtain calibration curve.

Figure 18-3.- Calibration curve data sheet - injection of volatile sample into Tedlar bag.

Rotameter number____________________

Gas used____________________

Method: Bubble meter______ Spirometer ______ Wet test meter______

Rotameter construction____________________

Float type ____________________

Laboratory temperature (T obs.) ________°C ________°F

Laboratory pressure (P obs.) ______in Hg ________ mm Hg

1.

Flowmeter reading	Time (min)	Gas volume[a]	Flow rate (lab conditions)[b]
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____

[a] Vol. of gas may be measured in milliliters, liters or cubic feet.

[b] Convert to standard conditions (20° C and 760 mm Hg).

$$Q_{STD} = Q_{obs} {\frac{760 \times T\ obs.}{P\ obs. \times 20}}^{1/2}$$

Flowmeter reading	Flow rate (STD conditions)
____	____
____	____
____	____
____	____
____	____
____	____

Plot meter reading against flow rate (std) and draw smooth curve.

Figure 18-4. Rotameter calibration data sheet.

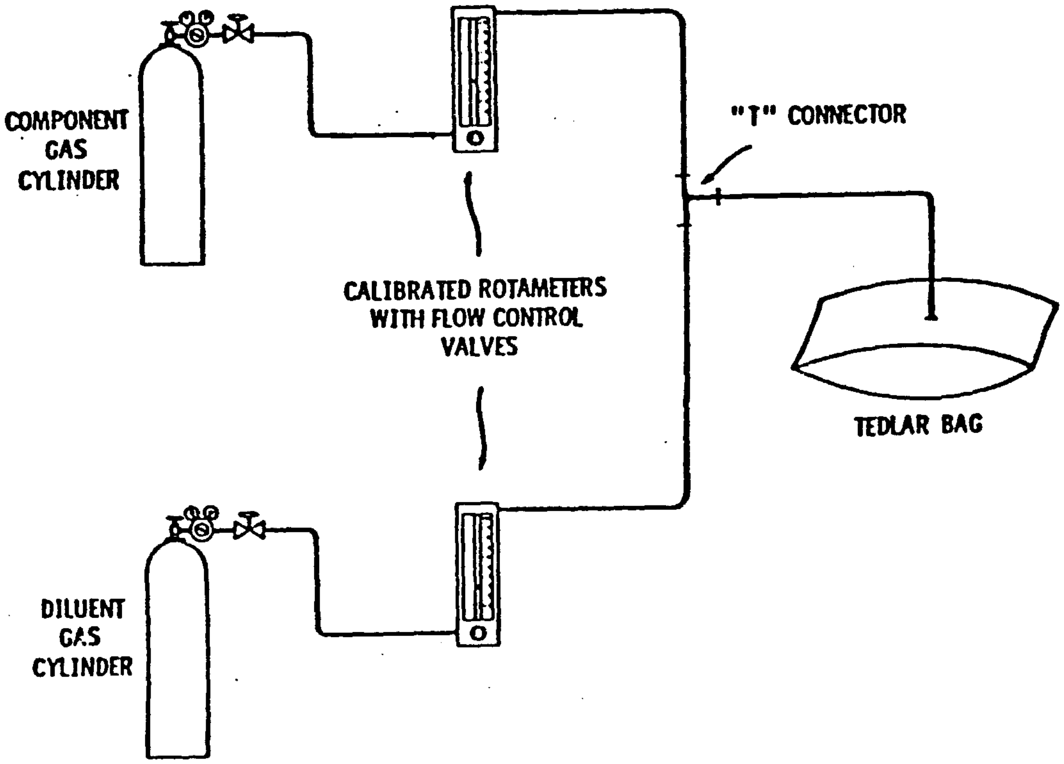

Figure 18-5. Single-stage calibration gas dilution system.

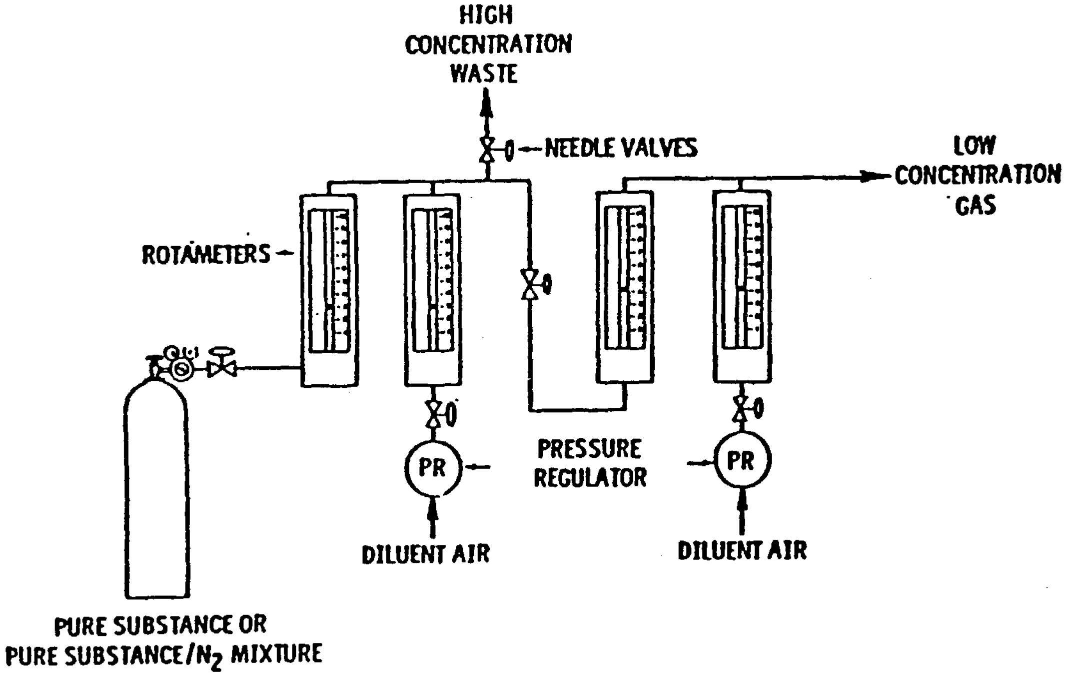

Figure 18-6. Two-stage dilution apparatus.

1. High concentration gas mixture

Component ____________ Concentration ___________ppm

Diluent gas ____________

2. Dilution and analysis data Date ___________

Stage 1	Mixture 1	Mixture 2	Mixture 3
Component gas-rotameter reading			
Diluent gas-rotameter reading			
Ambient temp. (°C)			
Manometer reading, inches H_2O			
Flow rate component gas (ml/min)			
Flow rate diluent gas (ml/min)			
Stage 2			
Component gas-rotameter reading			
Diluent gas-rotameter reading			
Flow rate component gas (ml/min)			
Flow rate diluent gas (ml/min)			
Calculated concentration (ppm)			
Analysis			
Sample loop volume (ml)			
Sample loop temp. (°C)			
Carrier gas flow rate (ml/min)			
Column temperature			
initial (°C)			
program rate (°C/min)			
final (°C)			
Injection time (24-hr. basis)			
Distance to peak (inches)			
Chart speed (inch/min)			
Retention time (min)			
Attenuator factor			
Peak height (mm)			
Peak area (mm^2)			
Area x attenuation factor (mm^2)			

Plot peak area x attenuator factor against concentration to obtain calibration curve.

Figure 18-7. Calibration curve data sheet - dilution method.

3. Low concentration standard

Known concentration (ppm)	
Retention time (min)	
Injection time (24-hour basis)	
Attenuation factor	
Peak height (mm)	
Peak area (mm^2)	
Peak area x attenuation (mm^2)	
Calculated concentration (ppm)	
Deviation (%)	

4. Audit samples	Sample 1	Sample 2
Retention time (min)		
Injection time 24-hour basis)		
Attenuation factor		
Peak height (mm)		
Peak area (mm^2)		
Peak area x attenuation factor		
Measured concentration		
Data reported on (date)		
Data reported by (initial)		
Certified concentration (ppm)		
Deviation (%)		

Note: If a pump is used instead of a rotameter for component gas flow, substitute pump delivery rate for rotameter readings).

Figure 18-7 (continued). Calibration curve data sheet - dilution method.

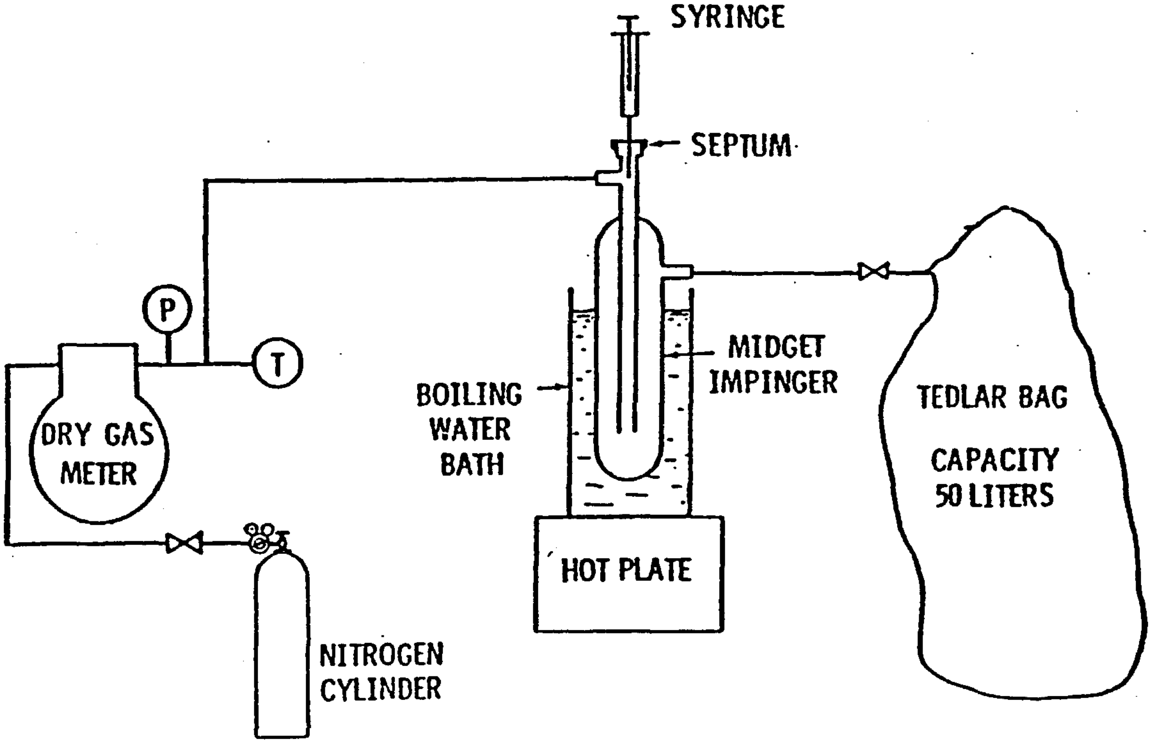

Figure 18-8. Apparatus for preparation of liquid materials.

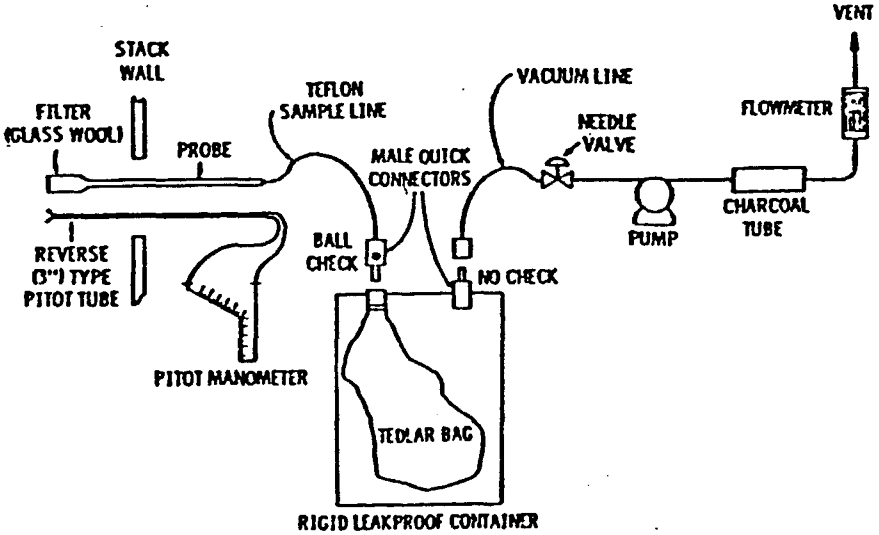

Figure 18-9. Integrated bag sampling train.

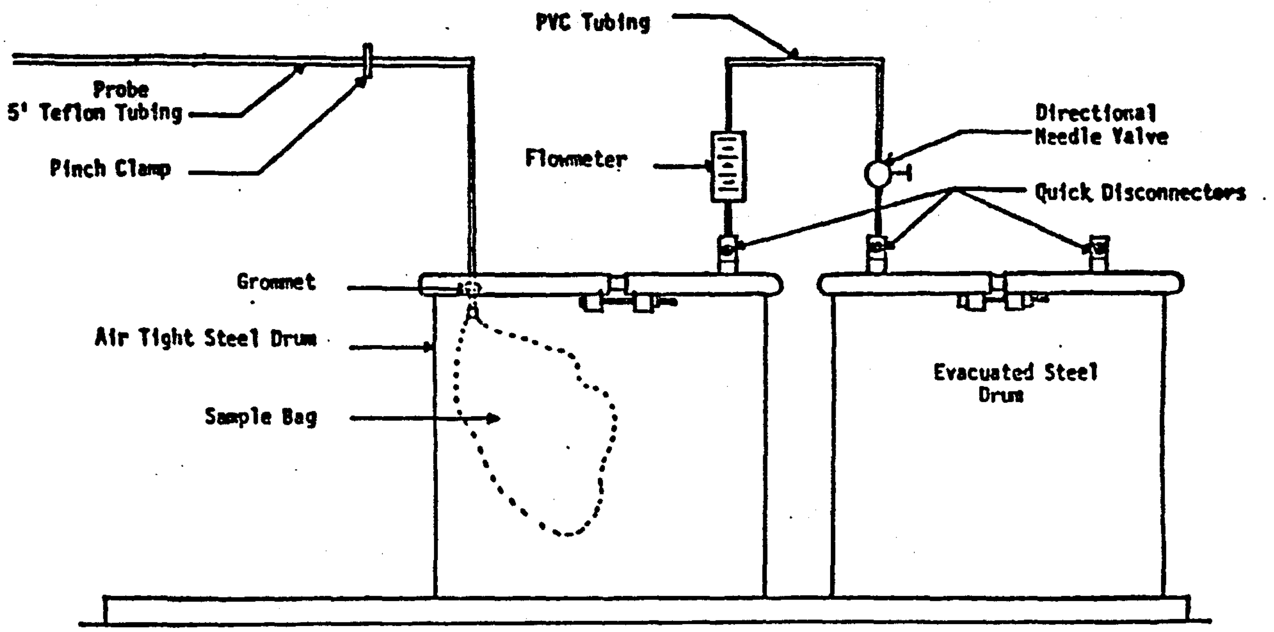

Figure 18-9a. Explosion risk gas sampling method.

Plant____________________ Date__________

Site________________________________

	Sample 1	Sample 2	Sample 3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18-10. Field sample data sheet - Tedlar bag collection method.

Plant
Date
Location

1. General information

Source temperature (°C)
Probe temperature (°C)
Ambient temperature (°C)
Atmospheric pressure (mm)
Source pressure ("Hg)
Absolute source pressure (mm)
Sampling rate (liter/min)
Sample loop volume (ml)
Sample loop temperature (°C)
Columnar temperature:
    Initial (°C)/time (min)
    Program rate (°C/min)
    Final (°C)/ time (min)
Carrier gas flow rate (ml/min)
Detector temperature (°C)
Injection time (24-hour basis)
Chart speed (mm/min)

Dilution gas flow rate (ml/min)
Dilution Gas used (symbol)
Dilution ratio

Figure 18-11. Field analysis data sheets.

2. Field Analysis Data - Calibration Gas

Run No.
Time

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No.
Time

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No.
Time

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Figure 18-11 (continued). Field analysis data sheets.

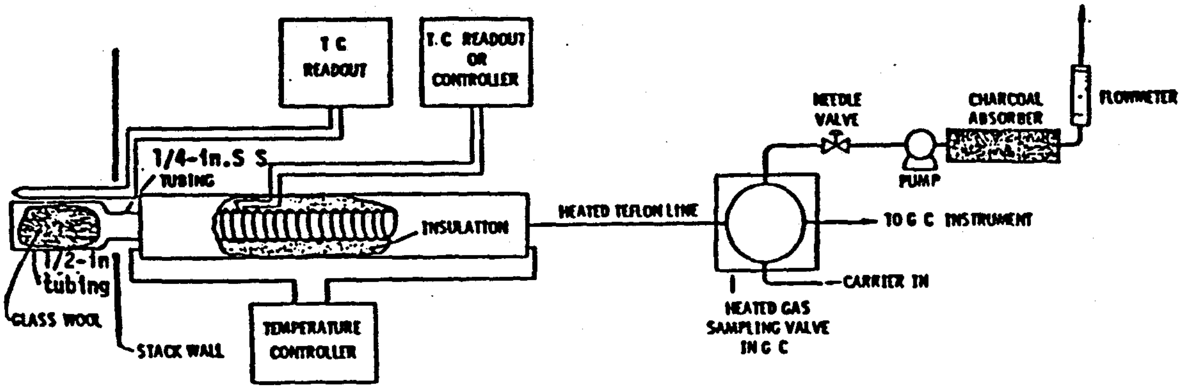

Figure 18-12. Direct interface sampling system.

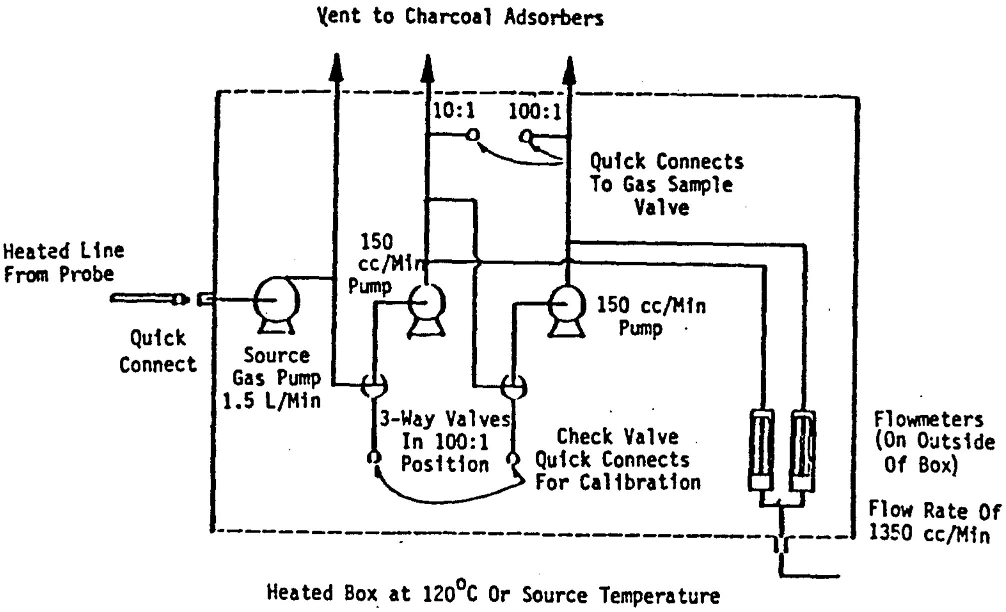

Figure 18-13. Schematic diagram of the heated box required for dilution of sample gas.

BILLING CODE 6560-50-C

Gaseous Organic Sampling and Analysis Check List

(Respond with initials or number as appropriate)

		Date
1. Presurvey data:		
A. Grab sample collected	☐	
B. Grab sample analyzed for composition	☐	
Method GC	☐	☐
GC/MS	☐	☐
Other	☐	☐
C. GC-FID analysis performed	☐	
2. Laboratory calibration data:		
A. Calibration curves prepared	☐	
Number of components	☐	☐
Number of concentrations/component (3 required)	☐	☐
B. Audit samples (optional):		
Analysis completed	☐	
Verified for concentration	☐	
OK obtained for field work	☐	
3. Sampling procedures:		
A. Method:		
Bag sample	☐	☐
Direct interface	☐	☐
Dilution interface	☐	☐
B. Number of samples collected	☐	
4. Field analysis:		
A. Total hydrocarbon analysis performed	☐	
B. Calibration curve prepared	☐	
Number of components	☐	☐
Number of concentrations per component (3 required)	☐	☐

Figure 18-14. Sampling and analysis check.

Gaseous Organic Sampling and Analysis Data

Plant—

Date—

Location—

	Source sample 1	Source sample 2	Source sample 3
1. General information:			
Source temperature (°C)			
Probe temperature (°C)			
Ambient temperature (°C)			
Atmospheric pressure (mm Hg)			
Source pressure (mm Hg)			
Sampling rate (ml/min)			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Sample collection time (24-hr basis)			
Column temperature:			
Initial (°C)			
Program rate (°C/min)			
Final (°C)			
Carrier gas flow rate (ml/min)			
Detector temperature (°C)			
Chart speed (cm/min)			
Dilution gas flow rate (ml/min)			
Diluent gas used (symbol)			
Dilution ratio			

Performed by (signature):

Date:

Figure 18-14. Sampling and analysis sheet.

6. In Appendix A of Part 60, the title of Method 22 is revised to read as follows:

Method 22—Visual Determination of Fugitive Emissions from Material Sources and Smoke Emissions from Flares.

7. In Appendix A of Part 60, Section 1 of Method 22, *Introduction*, is amended by adding the following sentence to the end of the first paragraph:

* * * * *

This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

8. In Appendix A of Part 60, Section 1 of Method 22, *Introduction*, is amended by removing the phrase "Reference Test" from the third sentence of the second paragraph.

9. In Appendix A of Part 60, Paragraph 2.1 of Section 2 of Method 22 is amended by adding a second paragraph as follows:

* * * * *

2.1 * * *

This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

* * * * *

10. In Appendix A of Part 60, Paragraph 2.2 of Section 2 of Method 22 is revised as follows:

* * * * *

2.2 *Principle.* Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

* * * * *

11. In Appendix A of Part 60, Method 22 Section 3, *Definitions*, Paragraphs 3.4 and 3.5 are revised to read as follows:

* * * * *

3.4 *Smoke Emissions.* Pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

3.5 *Observation Period.* Accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

* * * * *

12. In Appendix A of Part 60, Method 22 is amended by adding Figures 22-1 and 22-2 at the end of the method.

BILLING CODE 6560-50-M

FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company ____________ Observer ____________

Location ____________ Affiliation ____________

Company representative ____________ Date ____________

Sky Conditions ____________ Wind direction ____________

Precipitation ____________ Wind speed ____________

Industry ____________ Process unit ____________

Sketch process unit; indicate observer position relative to source and sun; indicate potential emission points and/or actual emission points.

OBSERVATIONS

	Clock time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation			
End observation			

Figure 22-1

Fugitive Emission Inspection Indoor Location Table

FUGITIVE EMISSION INSPECTION
INDOOR LOCATION

Company ____________ Observer ____________

Location ____________ Affiliation ____________

Company Representative ____________ Date ____________

Industry ____________ Process unit ____________

Light type (fluorescent, incandescent, natural ____________

Light location (overhead, behind observer, etc.) ____________

Illuminance (lux or footcandles) ____________

Sketch process unit; indicate observer position relative to source; indicate potential emission points and/or actual emission points.

OBSERVATIONS

	Clock time	Observation period duration, min:sec	Accumulated emission, time, min:sec
Beginning observation			
End observation			

Figure 22-2

[FR Doc. 83-27945 Filed 10-17-83; 8:45 am]
BILLING CODE 6560-50-C

504 METHOD 1400
NIOSH MANUAL OF ANALYTICAL METHODS
VOLUME 1
FEBRUARY 1984

FORMULA: Table 1

ALCOHOLS I

METHOD: 1400
ISSUED: 2/15/84

M.W.: Table 1

OSHA/NIOSH/ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS AND SYNONYMS:
(1) ethanol: [ethyl alcohol; CAS #64-17-5];
(2) isopropyl alcohol: [2-propanol; CAS #67-63-0]; and
(3) tert-butyl alcohol: [2-methyl-2-propanol; CAS #75-65-0].

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min (0.05 L/min for ethyl alcohol)

	(1)	(2)	(3)
VOL-MIN:	0.1 L	0.2 L	0.5 L
-MAX:	1 L	3 L	10 L

SHIPMENT: refrigerated

SAMPLE STABILITY: store in freezer; analyze as soon as possible

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 1% 2-butanol in CS_2

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 65 - 70 °C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 2 m x 4 mm ID, 0.2% Carbowax 1500 on 60/80 Carbopack C or equivalent

CALIBRATION: solutions of analyte in eluent with internal standard

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 mg per sample [4]

APPLICABILITY: This method employs a simple desorption and may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling efficiency. The methods were validated using a 3 m x 3 mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S56, S65 and S63 [3].

REAGENTS:

1. Eluent: Carbon disulfide* (chromatographic grade) with 1% (v/v) 2-butanol and 0.2% v/v n-undecane, 0.1% v/v ethyl benzene, or other suitable internal standard.
2. Analyte, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1400-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work with it must be done in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 0.1 to 1 L (ethanol), 0.2 to 3 L (isopropyl alcohol) or 0.5 to 10 L (t-butyl alcohol).
4. Cap the samplers with plastic (not rubber) caps and pack securely with bagged refrigerant for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.01 to 6 mg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.

b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
c. Cap the tube. Allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
e. Prepare a graph of DE vs. mg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1400-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S56, S65 and S63 were issued on January 17, 1975 [3], and validated using 1-, 3- and 10-L air samples, respectively, of atmospheres generated in dry air by calibrated syringe drive from absolute ethanol, 2-propanol and t-butyl alcohol [1]. Overall precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision (s_r)	Recovery (%)	Range Studied mg/m³	Range Studied mg per sample	Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision (s_r)
S56	0.065	103.6	900 to 3300	1 to 4	1.6 L	0.79*	0.027
S65	0.064	96.7	505 to 1890	1 to 5	6.0 L	0.93*	0.033
S63	0.075	100.3	165 to 600	1.5 to 6	17.0 L	0.91*	0.018

*Over the range studied. Each laboratory must do their own DE determinations.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, (NIOSH) Publication No. 77-185 (1977).

[2] White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Am. Ind. Hyg. Assoc. J., 31:225 (1970).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S56, S65 and S63, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] User check, UBTL, NIOSH Sequence #3990-S (unpublished, November 3, 1983).

METHOD REVISED BY: George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contract 99-74-45.

Table 1. General information.

Compound	OSHA NIOSH ACGIH (ppm)	Formula	mg/m³ = 1 ppm @ NTP	M.W.	Density @ 20 °C (g/mL)	BP (°C)	VP @ 20 °C, kPa (mm Hg)
Ethanol	1000 — 1000	CH_3CH_2OH; C_2H_6O	1.883	46.07	0.789	78.5	5.6 (42)
Isopropyl alcohol	400 400 500	$CH_3CH(OH)CH_3$; C_3H_8O	2.46	60.09	0.785	82.5	4.4 (33)
tert-Butyl alcohol	100 100 150	$(CH_3)_3COH$; $C_4H_{10}O$	3.03	74.12	0.786	82.4; MP = 25.6 °C	4.1 (31)

505 ENVIRONMENTAL PROTECTION AGENCY
METHOD 8240
"GC/MS METHOD FOR VOLATILE ORGANICS"
DECEMBER 1987

METHOD 8240

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds may be determined by this method:

Analyte	CAS No.[b]	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	pp	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	pp	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
2-Butanone	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chlorobenzene	108-90-7	a	a
Chlorobenzene-d_5 (I.S.)	108-90-7	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropionitrile	562-76-7	ND	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a
Dibromomethane	74-95-3	a	a
1,4-Dichloro-2-butene	764-41-0	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a

		Appropriate Technique	
Analyte	CAS No.[b]	Purge-and-Trap	Direct Injection
1,2-Dichloroethane	107-06-2	a	a
1,2-Dichloroethane-d_4(surr.)	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2:3,4-Diepoxybutane	1464-53-5	a	a
1,4-Difluorobenzene (I.S.)	123-91-1	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-10-5	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	ND	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone	108-10-1	pp	a
Pentachloroethane	76-01-7	i	pc
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
b-Propiolactone	57-57-8	pp	a
Propionitrile	107-12-0	pp	a
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
Toluene-d_8 (surr.)	108-88-3	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a
1,2,3-Trichloropropane	96-18-4	a	a
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
Xylene (Total)	1330-20-7	a	a

[a] Adequate response by this technique.
[b] Chemical Abstract Services Registry Number.
[pp] Poor purging efficiency resulting in high PQLs.
[i] Inappropriate technique for this analyte.
[pc] Poor chromatographic behavior.

1.2 Method 8240 can be used to quantify most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique, however, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The practical quantitation limit (PQL) of Method 8240 for an individual compound is approximately 5 ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 ug/L for ground water (see Table 2). PQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A field blank prepared from ASTM Type II water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of reagent water to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running calibration and reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10-uL, 25-uL, 100-uL, 250-uL, 500-uL, and 1,000 uL. These syringes should be equipped with a 20-gauge (0.006-in i.d.) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5-mL, gas-tight with shutoff valve.

4.4 Balance - Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.5 Glass scintillation vials - 20-mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

4.6 Volumetric flasks - 10-mL and 100-mL, class A with ground-glass stoppers.

4.7 Vials - 2-mL, for GC autosampler.

4.8 Spatula - Stainless steel.

4.9 Disposable pipets - Pasteur.

4.10 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed

220°C during bake-out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 Trap Packing Materials

4.11.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

4.12 Gas chromatograph/mass spectrometer system

4.12.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 Column - 6-ft x 0.1-in. i.d. glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer - Capable of scanning from 35-260 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. Must be free of interferences at the method detection limit (MDL) of the analytes of interest. ASTM Type II water is further purified by any of the following techniques:

5.2.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Milli-Q Plus with the Organex-Q cartridge or equivalent) may be used to generate reagent water.

5.2.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hour. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.3 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.3.1 Place about 9.8 mL of methanol in a 10-mL tared ground- glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Add the assayed reference material, as described below.

5.3.2.1 Liquids - Using a 100-ul syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum

(#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a Teflon-sealed screw cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.3.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.4 Secondary dilution standards - Using stock standard solutions, prepare in methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Step 5.1, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 ug/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 uL of the surrogate spiking solution prior to analysis.

5.6 Internal standards - The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Steps 5.1 and 5.2. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 ug/mL of each internal standard compound. Addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ug/L.

5.7 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/uL of BFB in methanol should be prepared.

5.8 Calibration standards - Calibration standards at a minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Steps 5.1 and 5.2). Prepare these solutions in water. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Calibration standards must be prepared daily.

5.9 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 ug/10.0 mL.

5.10 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at -10°C to -20°C in screw-cap amber bottles with Teflon liners.

5.11 Methanol, CH_3OH. Pesticide quality or equivalent. Store apart from other solvents.

5.12 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.12.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed is a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two-stage methanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 0.1 mg/mL of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw-cap bottle in an area that is not contaminated by solvent vapors.

5.12.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, a water/tetraglyme blank must be analyzed.

5.13 Polyethylene glycol, $H(OCH_2CH_2)_nOH$. Free of interferences at the detection limit of the analytes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Recommended GC/MS operating conditions

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak but not to exceed 7 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 minutes
Column temperature program:	8°C/minutes
Final column temperature:	220°C.
Final column holding time:	15 minutes
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.2.2 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection or purging of 4-bromofluorobenzene (2-uL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Step 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device (use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of water to the purging device. The water is added to the purging device using a 5-mL glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-uL or 25-uL micro-syringe equipped with a long needle (Step 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Step 5.6). Add the aliquot of calibration solution directly to the reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 uL of the internal standard solution (Step 5.4). Close the 2-way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Step 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Step 7.5.2). The RF is calculated as follows:

$$RF = (A_xC_{is})/(A_{is}C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

7.2.8 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

7.2.8.3 Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.9 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs).

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = relative standard deviation.

$\bar{x}$ = mean of 5 initial RFs for a compound.

SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

The %RSD for each individual CCC should be <u>less</u> than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50-ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift.

7.3.2 The initial calibration curve (Step 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Step 7.3.3) and CCC (Step 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Step 7.2.9 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\%\ \text{Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (> 25% difference), for any one CCC, corrective action <u>MUST</u> be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration <u>MUST</u> be generated. This criterion <u>MUST</u> be met before quantitative sample analysis begins.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (- 50% to + 100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (ECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Step 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Step 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Step 7.2.8).

7.4.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within

24 hours. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10-to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Step 7.4.1.6 into the flask. Aliquots of less than 1-mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5-mL syringe with the diluted sample as in Step 7.4.1.6.

7.4.1.8 Add 10.0 uL of surrogate spiking solution (Step 5.3) and 10 uL of internal standard spiking solution (Step 5.4) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of water (or methanol followed by water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 uL of the matrix spike solution (Step 5.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Steps 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water-miscible liquids

7.4.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with reagent water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose.

These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (> 1 mg/kg).

7.4.3.1 Low-level method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5-g sample if the expected concentration is < 0.1 mg/kg or a 1-g sample for expected concentrations between 0.1 and 1 mg/kg.

7.4.3.1.2 The GC/MS system should be set up as in Steps 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution (Step 5.3) and internal standard solution (Step 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 uL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 ug/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the <u>entire</u> contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Step 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1 g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\% \text{ moisture} = \frac{\text{grams of sample} - \text{grams of dry sample}}{\text{grams of sample}} \times 100$$

7.4.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Steps 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minute.

7.4.3.1.8 Proceed with the analysis as outlined in Steps 7.4.1.11-7.4.1.16. Use 5 mL of the same water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the medium-level method must be followed.

7.4.3.1.9 For low-level sediment/soils add 10 uL of the matrix spike solution (Step 5.7) to the 5 mL of water (Step 7.4.3.1.3). The concentration for a 5-g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.4.3.2 High-level method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to reagent water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Step 7.4.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

<u>NOTE</u>: Steps 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100-uL aliquot of each of these extracts in Step 7.4.3.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Steps 7.4.1.2-7.4.1.4. This should be done prior to the addition of the solvent extract to water.

7.4.3.2.5 Table 4 can be used to determine the volume of solvent extract to add to the 5 mL of water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a medium-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 uL of internal standard solution. Also add the volume of solvent extract determined in Step 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 uL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Step 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 uL of solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the medium-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Step 5.3), and 1.0 mL of matrix spike solution (Step 5.7) as in Step 7.4.3.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4-g sample. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Step 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 An analyte (e.g. those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.5.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.5.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% <u>must</u> be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 5).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Step 7.2.7).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste

High-level

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-level

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = same as for water.

V_t = volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).

V_i = volume of extract added (uL) for purging.

W_s = weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample (as calculated in Step 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.5 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a calibration blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Step 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Step 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Step 7.3.3 and the CCC criteria in Step 7.3.4, each 12 hours.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 ug/mL in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC reference sample to contain 20 ug/L of each analyte by adding 200 uL of QC reference sample concentrate to 100 mL of water.

8.5.3 Four 5-mL aliquots of the well-mixed QC reference sample are analyzed according to the method beginning in Step 7.4.1.

8.5.4 Calculate the average recovery (x) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

8.5.5 For each analyte compare s and x with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and x for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual x falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Step 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Step 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank and a spiked replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a specific limit, the spike should be at 20 ug/L or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger. For other matrices, recommended spiking concentration is 10 times the PQL.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.5.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be acounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Step 8.7.

8.7 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.6, a QC reference sample containing each analyte that failed must be prepared and analyzed.

<u>NOTE</u>: The frequency for the required analysis of a QC reference sample will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Step 8.6, the probability that the analysis of a QC reference sample will be required is high. In this case the QC reference sample should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 10 uL of the QC reference sample concentrate (Step 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC reference sample needs only to contain the analytes that failed criteria in the test in Step 8.6.

8.7.2 Analyze the QC reference sample to determine the concentration measured (A) of each analyte. Calculate each precent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Step 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = $p + 3s$
Lower Control Limit (LCL) = $p - 3s$

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

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TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Ethylene oxide	1.30	44	44,43,42
Chloromethane	2.30	50	52,49
Dichlorodifluoromethane	2.47	85	85,87,101,103
Bromomethane	3.10	94	96,79
Vinyl chloride	3.80	62	64,61
Acetonitrile	3.97	41	41,40,39
Chloroethane	4.60	64	66,49
Methyl iodide	5.37	142	142,127,141
Methylene chloride	6.40	84	49,51,86
Carbon disulfide	7.47	76	76,78,44
Trichlorofluoromethane	8.30	101	103,66
Propionitrile	8.53	54	54,52,55,40
Allyl chloride	8.83	76	76, 41, 39, 78
1,1-Dichloroethene	9.00	96	61, 98
Bromochloromethane (I.S.)	9.30	128	49, 130, 51
Allyl alcohol	9.77	57	57,58,39
trans-1,2-Dichloroethene	10.00	96	61,98
1,2-Dichloroethane	10.10	62	64,98
Propargyl alcohol	10.77	55	55,39,38,53
Chloroform	11.40	83	85,47
1,2-Dichloroethane-d_4(surr)	12.10	65	102
2-Butanone	12.20	72	43,72
Methacrylonitrile	12.37	41	41,67,39,52,66
Dibromomethane	12.53	93	93,174,95,172,176
2-Chloroethanol	12.93	49	49,44,43,51,80
b-Propiolactone	13.00	42	42,43,44
Epichlorohydrin	13.10	57	57,49,62,51
1,1,1-Trichloroethane	13.40	97	99,117
Carbon tetrachloride	13.70	117	119,121
1,4-Dioxane	13.70	88	88,58,43,57
Isobutyl alcohol	13.80	43	43,41,42,74
Bromodichloromethane	14.30	83	85,129
Chloroprene	14.77	53	53,88,90,51
1,2:3,4-Diepoxybutane	14.87	55	55,57,56
1,2-Dichloropropane	15.70	63	62,41
cis-1,3-Dichloropropene	15.90	75	77,39
Bromoacetone	16.33	136	43,136,138,93,95
Trichloroethene	16.50	130	95,97,132
Benzene	17.00	78	52,71
trans-1,3-Dichloropropene	17.20	75	77,39
1,1,2-Trichloroethane	17.20	97	83,85,99
3-Chloropropionitrile	17.37	54	54,49,89,91
1,2-Dibromoethane	18.40	107	107,109,93,188
Pyridine	18.57	79	79,52,51,50

TABLE 1.
(Continued)

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
2-Chloroethyl vinyl ether	18.60	63	65,106
2-Hydroxypropionitrile	18.97	44	44,43,42,53
1,4-Difluorobenzene (I.S.)	19.60	114	63,88
Malononitrile	19.60	66	66,39,65,38
Methylmethacrylate	19.77	69	69,41,100,39
Bromoform	19.80	173	171,175,252
1,1,1,2-Tetrachloroethane	20.33	131	131,133,117,119,95
1,3-Dichloro-2-propanol	21.83	79	79,43,81,49
1,1,2,2-Tetrachloroethane	22.10	83	85,131,133
Tetrachloroethene	22.20	164	129,131,166
1,2,3-Trichloropropane	22.20	75	75,77,110,112,97
1,4-Dichloro-2-butene	22.73	75	75,53,77,124,89
n-Propylamine	23.00	59	59,41,39
2-Picoline	23.20	93	93,66,92,78
Toluene	23.50	92	91,65
Ethyl methacrylate	23.53	69	69,41,99,86,114
Chlorobenzene	24.60	112	114,77
Pentachloroethane[a]	24.83	167	167,130,132,165,169
Ethylbenzene	26.40	106	91
1,2-Dibromo-3-chloropropane	27.23	157	157,75,155,77
4-Bromofluorobenzene (surr.)	28.30	95	174,176
Benzyl chloride	29.50	91	91,126,65,128
Styrene	30.83	104	104,103,78,51,77
Acetone	--	43	58
Acrolein	--	56	55,58
Acrylonitrile	--	53	52,51
Chlorobenzene-d_5 (I.S.)	--	117	82,119
Chlorodibromomethane	--	129	208,206
1,1-Dichloroethane	--	63	65,83
Ethanol	--	31	45,27,46
2-Hexanone	--	43	58,57, 100
Iodomethane	--	142	127,141
4-Methyl-2-pentanone	--	43	58,57,100
Toluene-d_8 (surr.)	--	98	70,100
Vinyl acetate	--	43	86
Xylene (Total)	--	106	91

[a] The base peak at m/e 117 was not used due to an interference at that mass with a nearly coeluting internal standard, chlorobenzene-d_5.

TABLE 2.
PRACTICAL QUATITATION LIMITS (PQL) FOR VOLATILE ORGANICS[a]

	Practical Quantitation Limits[b]	
	Ground water	Low Soil/Sediment
Volatiles	ug/L	ug/kg
Acetone	100	100
Acetonitrile	100	100
Allyl chloride	5	5
Benzene	5	5
Benzyl chloride	100	100
Bromodichloromethane	5	5
Bromoform	5	5
Bromomethane	10	10
2-Butanone	100	100
Carbon disulfide	100	100
Carbon tetrachloride	5	5
Chlorobenzene	5	5
Chlorodibromomethane	5	5
Chloroethane	10	10
2-Chloroethyl vinyl ether	10	10
Chloroform	5	5
Chloromethane	10	10
Chloroprene	5	5
1,2-Dibromo-3-chloropropane	100	100
1,2-Dibromoethane	5	5
Dibromomethane	5	5
1,4-Dichloro-2-butene	100	100
Dichlorodifluoromethane	5	5
1,1-Dichloroethane	5	5
1,2-Dichloroethane	5	5
1,1 Dichloroethene	5	5
trans-1,2-Dichloroethene	5	5
1,2-Dichloropropane	5	5
cis-1,3-Dichloropropene	5	5
trans-1,3-Dichloropropene	5	5
Ethylbenzene	5	5
Ethyl methacrylate	5	5
2-Hexanone	50	50
Isobutyl alcohol	100	100
Methacrylonitrile	100	100
Methylene chloride	5	5
Methyl iodide	5	5
Methyl methacrylate	5	50
4-Methyl-2-pentanone	50	50
Pentachloroethane	10	10

TABLE 2.
(Continued)

Volatiles	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/kg
Propionitrile	100	100
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
1,1,1-Trichloroethane	5	5
1,1,2-Trichloroethane	5	5
Trichloroethene	5	5
1,2,3-Trichloropropane	5	5
Vinyl acetate	50	50
Vinyl chloride	10	10
Xylene (Total)	5	5

[a] Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable. See the following information for further guidance on matrix-dependent PQLs.

[b] PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on the percent moisture in each sample.

Other Matrices:	Factor[1]
Water miscible liquid waste	50
High-level soil & sludges	125
Non-water miscible waste	500

[1] PQL = [PQL for ground water (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF MEDIUM-LEVEL SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500- 10,000 ug/kg	100 uL
1,000- 20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

[b] Dilute and aliquot of the methanol extract and then take 100 uL for analysis.

TABLE 5.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane

Acetone
Acrolein
Acrylonitrile
Bromomethane
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,2-Dichloroethane-d_4 (surrogate)
1,1-Dichloroethene
trans-1,2-Dichloroethene
Iodomethane
Methylene chloride
Trichlorofluoromethane
Vinyl chloride

1,4-Difluorobenzene

Benzene
Bromodichloromethane
Bromoform
2-Butanone
Carbon tetrachloride
Chlorodibromomethane
2-Chloroethyl vinyl ether
Dibromomethane
1,4-Dichloro-2-butene
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Vinyl acetate

Chlorobenzene-d_5

Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

TABLE 6.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for s (ug/L)	Range for x (ug/L)	Range p, p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in ug/L.
s = Standard deviation of four recovery measurements, in ug/L.
x = Average recovery for four recovery measurements, in ug/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

[a] Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 ug/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Benzene	0.93C+2.00	0.26x-1.74	0.25x-1.33
Bromodichloromethane	1.03C-1.58	0.15x+0.59	0.20x+1.13
Bromoform	1.18C-2.35	0.12x+0.34	0.17x+1.38
Bromomethane	1.00C	0.43x	0.58x
Carbon tetrachloride	1.10C-1.68	0.12x+0.25	0.11x+0.37
Chlorobenzene	0.98C+2.28	0.16x-0.09	0.26x-1.92
Chloroethane	1.18C+0.81	0.14x+2.78	0.29x+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62x	0.84x
Chloroform	0.93C+0.33	0.16x+0.22	0.18x+0.16
Chloromethane	1.03C-1.81	0.37x+2.14	0.58x+0.43
Dibromochloromethane	1.01C-0.03	0.17x-0.18	0.17x+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22x-1.45	0.30x-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14x-0.48	0.18x-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22x-1.45	0.30x-1.20
1,1-Dichloroethane	1.05C+0.36	0.13x-0.05	0.16x+0.47
1,2-Dichloroethane	1.02C+0.45	0.17x-0.32	0.21x-0.38
1,1-Dichloroethene	1.12C+0.61	0.17x+1.06	0.43x-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14x+0.09	0.19x+0.17
1,2-Dichloropropane[a]	1.00C	0.33x	0.45x
cis-1,3-Dichloropropene[a]	1.00C	0.38x	0.52x
trans-1,3-Dichloropropene[a]	1.00C	0.25x	0.34x
Ethyl benzene	0.98C+2.48	0.14x+1.00	0.26x-1.72
Methylene chloride	0.87C+1.88	0.15x+1.07	0.32x+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16x+0.69	0.20x+0.41
Tetrachloroethene	1.06C+0.60	0.13x-0.18	0.16x-0.45
Toluene	0.98C+2.03	0.15x-0.71	0.22x-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12x-0.15	0.21x-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14x+0.02	0.18x+0.00
Trichloroethene	1.04C+2.27	0.13x+0.36	0.12x+0.59
Trichlorofluoromethane	0.99C+0.39	0.33x-1.48	0.34x-0.39
Vinyl chloride	1.00C	0.48x	0.65x

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of x, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in ug/L.

C = True value for the concentration, in ug/L.

x = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

[a] Estimates based upon the performance in a single laboratory.

[b] Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

FIGURE 1.
PURGING CHAMBER

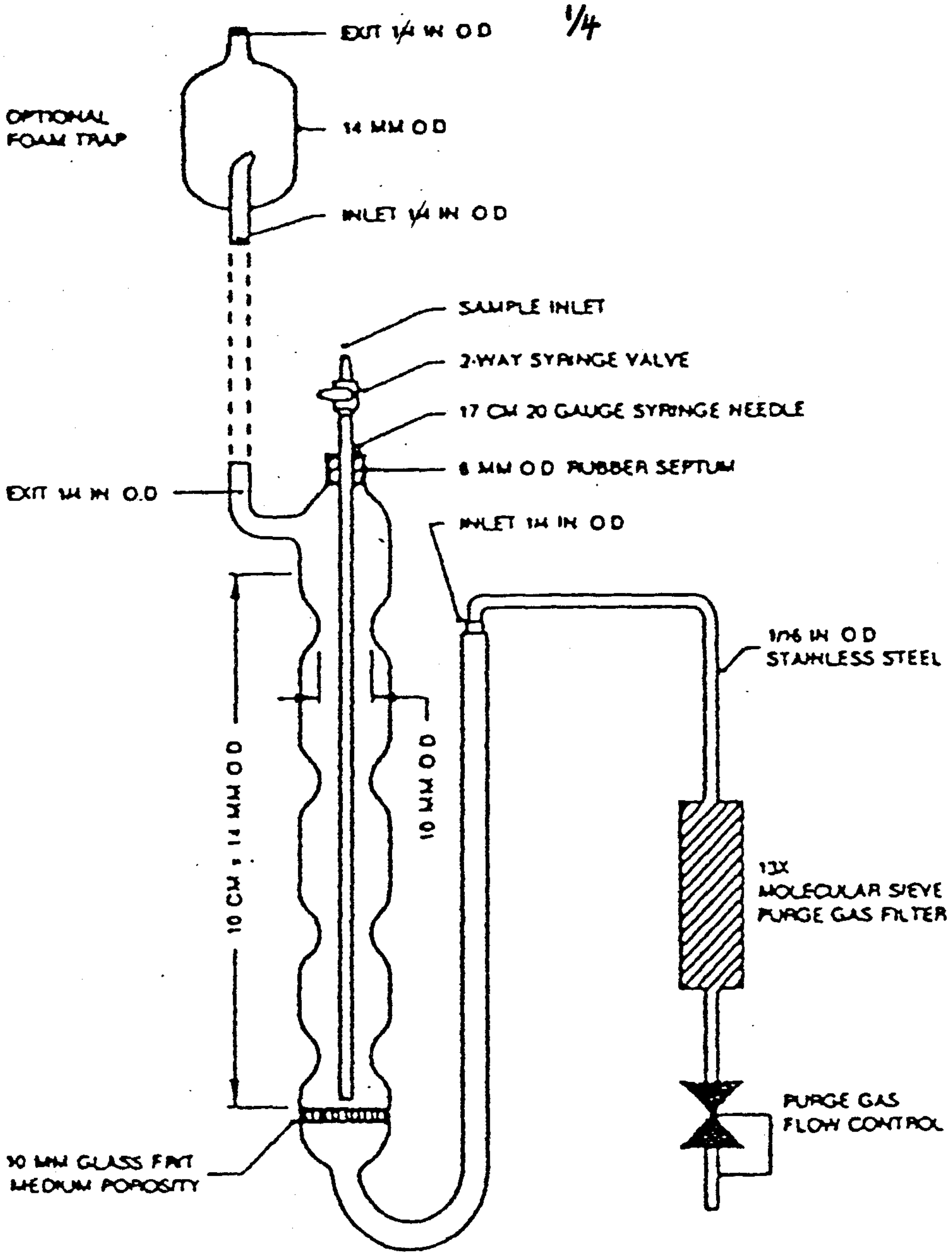


FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY FOR METHOD 8240

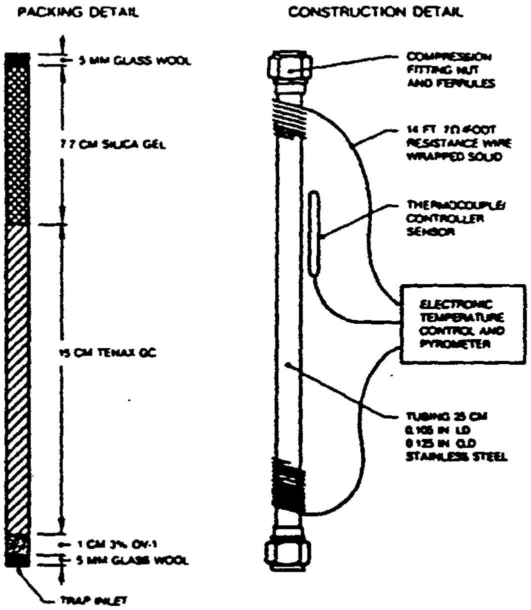
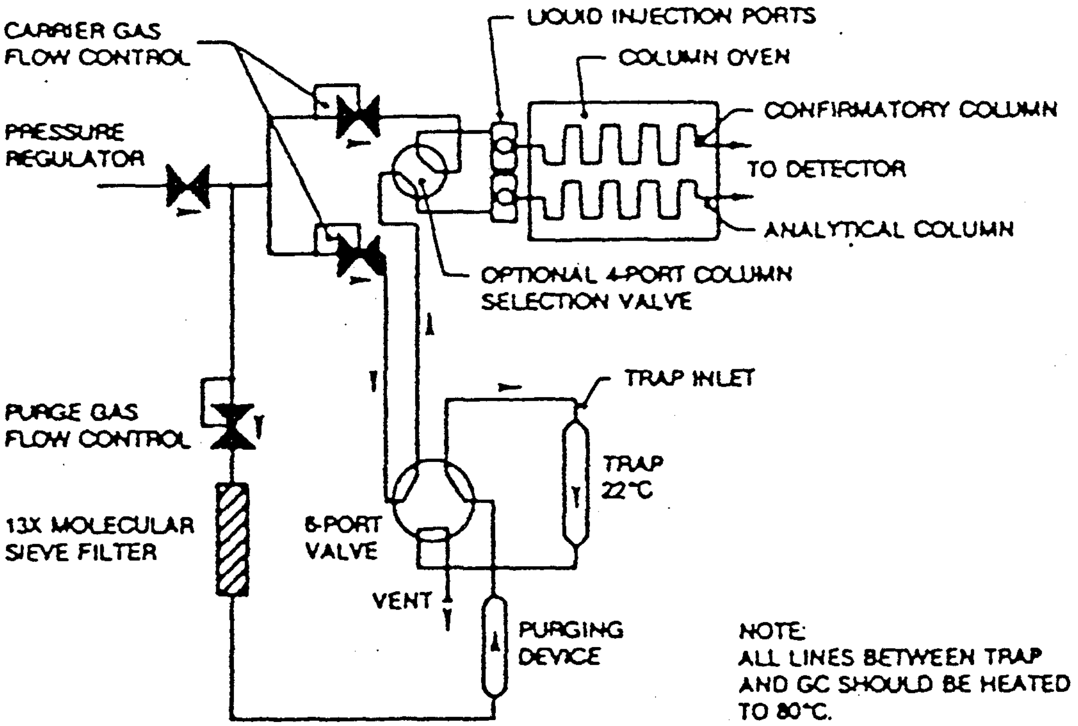


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE FOR METHOD 8240



NOTE:
ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 80°C.

FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE FOR METHOD 8240

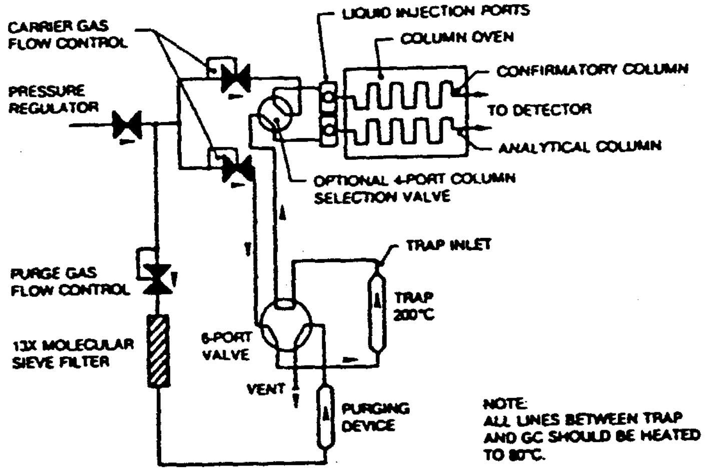
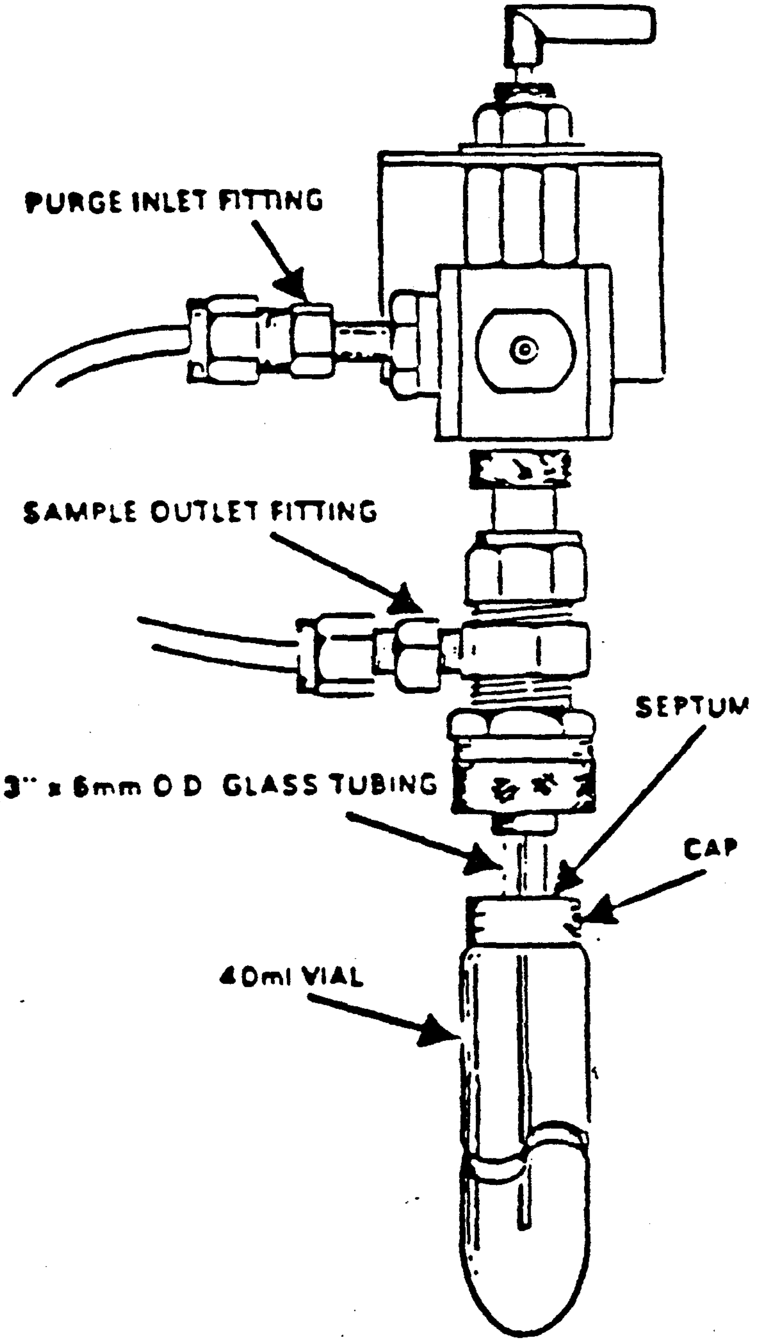
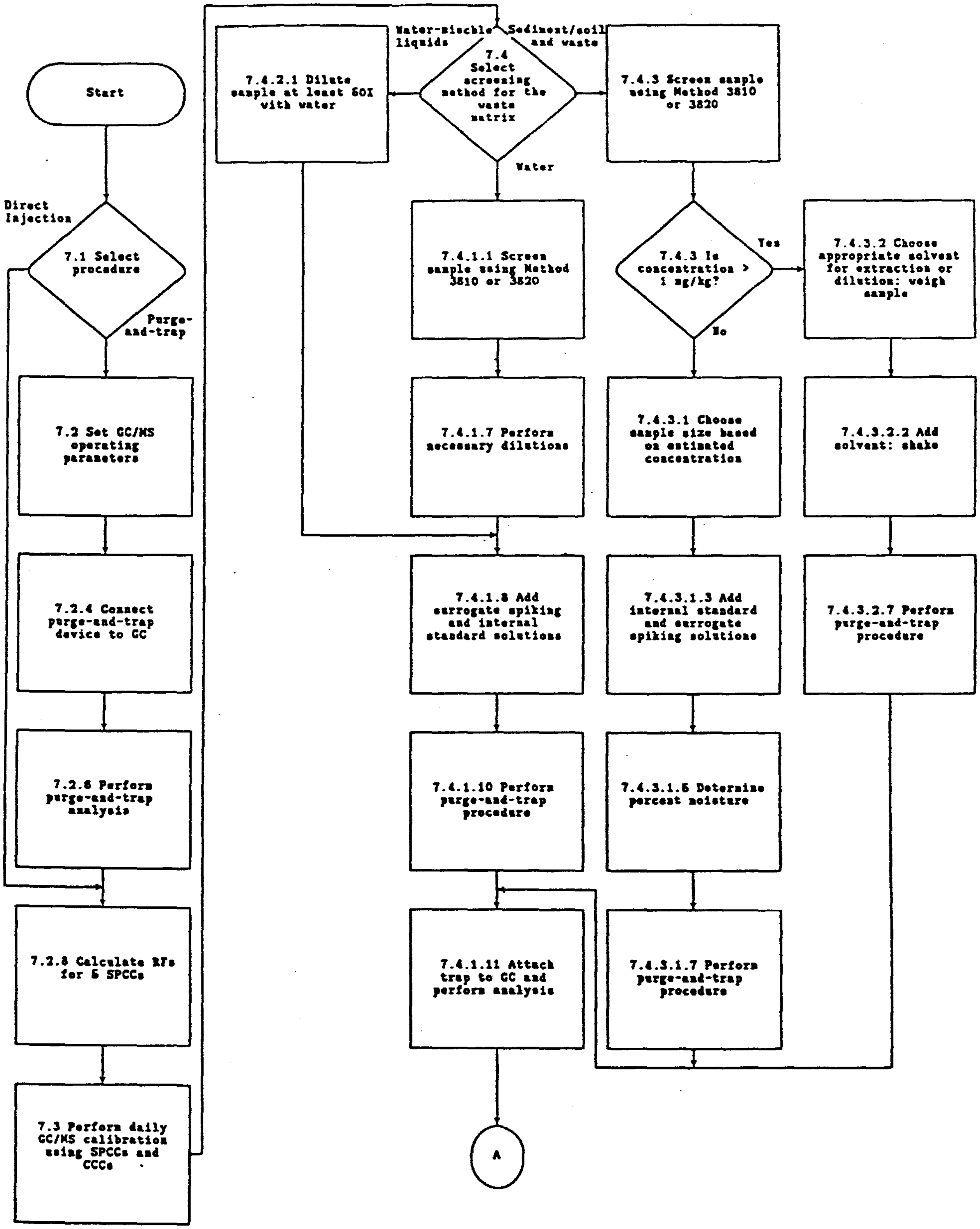
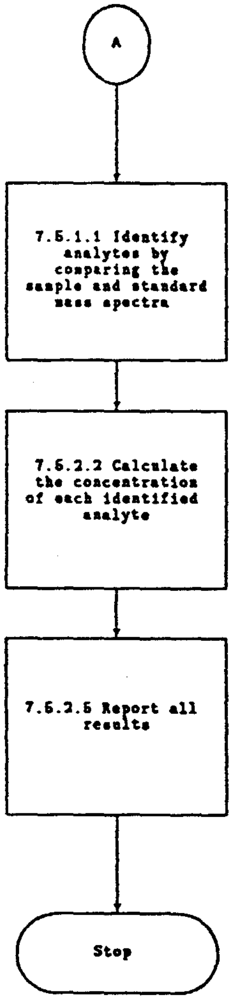


FIGURE 5.
LOW SOILS IMPINGER



METHOD 8240
GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS




A
7.5.1.1 Identify analytes by comparing the sample and standard mass spectra
7.6.2.2 Calculate the concentration of each identified analyte
7.6.2.5 Report all results
Stop

506 DEMONSTRATION METHOD

"Testing to determine compliance with the requirements of this article may also be demonstrated through calculation of the volatile organic compound content from records of the amounts of constituents used to make the product. Compliance determination based on these records may not be used unless the manufacturer of a consumer product keeps accurate records for each day of production of the amount and chemical composition of the individual product constituents. These records must be kept for at least three years." California Code of Regulations sections 94506 (b) and 94515 (b).

During inspection, for example, an inspector may ask to see production records pertaining to particular product samples obtained from a retailer's shelf. Considerations could then be given to the composition of the raw materials, biproducts, and wastes to assess the resulting VOC content of that final product.