

# VOC Sampling and Analysis Workshop

## Volume I VOC Reference Methods



# **VOC Sampling and Analysis Workshop**

## **Volume I. VOC Reference Methods**

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**Prepared for**

**U.S. ENVIRONMENTAL PROTECTION AGENCY  
Office of Air Quality Planning and Standards  
Stationary Source Compliance Division  
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## INTENDED PURPOSE

This is not an official policy and standards document. The opinions, findings, and conclusions are those of the authors and not necessarily those of the Environmental Protection Agency. Every attempt has been made to represent the present state of the art as well as subject areas still under evaluation. Many of the VOC methods contained in this manual are either draft methods or guideline procedures. Since any draft method is subject to change and even elimination, none of the material presented should be used as an EPA policy or recommendation unless it is a promulgated EPA reference method. The methods are included as training material only. Any mention of products or organizations does not constitute endorsement by the United States Environmental Protection Agency.

This document is issued by the Stationary Source Compliance Division, Office of Air Quality Planning and Standards, USEPA. It is for use in workshops presented by Agency staff and others receiving contractual or grant support from the USEPA. It is part of a series of instructional manuals addressing VOC compliance testing procedures.

Governmental air pollution control agencies establishing training programs may receive single copies of this document, free of charge, from the Stationary Source Compliance Division Workshop Coordinator, USEPA, MD-7, Research Triangle Park, NC 27711. Since the document is specially designed to be used in conjunction with other training materials and will be updated and revised as needed periodically, it is not issued as an EPA publication nor copies maintained for public distribution.

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## 1. Applicability and Principle

The applicability and principle of this method are identical to Method 1, except its applicability is limited to stacks or ducts less than about 0.30 meter (12 in.) in diameter, or  $0.071 \text{ m}^2$  (113 in.<sup>2</sup>) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter, or  $0.0081 \text{ m}^2$  (12.57 in.<sup>2</sup>) in cross-sectional area.

In these small diameter stacks or ducts the conventional pitot assembly (consisting of a Type S pitot tube attached to a sampling probe, equipped with a nozzle and thermocouple) blocks a significant cross-section of the duct and prevents a true traverse. Therefore, for particulate sampling in small stacks or ducts, the gas velocity is measured using a standard pitot tube downstream of the actual emission testing site. The straight run of duct between the sampling and velocity measurement sites allows the flow profile, temporarily disturbed by the presence of the sampling probe, to redevelop and stabilize.

The cross-sectional layout and location of traverse points and the verification of the absence of cyclonic flow are the same as in Method 1, Sections 2.3 and 2.4, respectively. Differences from Method 1, except as noted, are given below.

## 2. Procedure

### 2.1 Selection of Measurement Site.

2.1.1 Particulate Traverses - Steady or Unsteady Flow. Select a particulate measurement site located preferably at least eight equivalent stack or duct diameters downstream and ten equivalent diameters upstream from any flow disturbance such as a bend, expansion, or contraction in the stack,

or from a visible flame. Locate the velocity measurement site 8 equivalent diameters downstream of the particulate measurement site. See Figure 1A-1. If such locations are not available, select an alternative particulate measurement location at least two equivalent stack or duct diameters downstream and two and one-half diameters upstream from any flow disturbance. Locate the velocity measurement site 2 equivalent diameters downstream from the particulate measurement site. (See Section 2.1 of Method 1 for calculating equivalent diameters for a rectangular cross-section.)

2.1.2 Particulate (Steady Flow) or Velocity (Steady or Unsteady Flow) Measurements. If the average total volumetric flow rate in a duct is constant with respect to time or if only velocity measurements are required use the same criterion as in Section 2.1 of Method 1.

## 2.2 Determining the Number of Traverse Points.

2.2.1 Particulate Measurements (Steady or Unsteady Flow). Use Figure 1A-2 to determine the number of traverse points. Before referring to the figure, however, determine the distance between the velocity and sampling sites and the distances to the nearest upstream and downstream disturbances and divide each distance by the stack diameter or equivalent diameter to determine the distances in terms of the number of duct diameters. Then, determine the number of traverse points from Figure 1A-2 corresponding to each of these three distances. Choose the highest of the three numbers of traverse points (or a greater number) so that for circular ducts the number is a multiple of 4; for rectangular ducts use one of those numbers shown in Table 1-1 of Method 1.

2.2.2 Particulate (Steady Flow) and Velocity (Non-Particulate) Measurements. Use Figure 1A-3 to determine number of traverse points, following the same procedure used for particulate traverses as described in Section 2.2.1 of Method 1.

### 3. Bibliography

1. Same as Method 1, Section 3, Citations 1 through 6.
2. Vollaro, Robert F. Recommended Procedure for Sample Traverses in Ducts Smaller Than 12 Inches in Diameter. U. S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, NC. January 1977.

## RECOMMENDED SAMPLING ARRANGEMENT FOR SMALL DUCTS

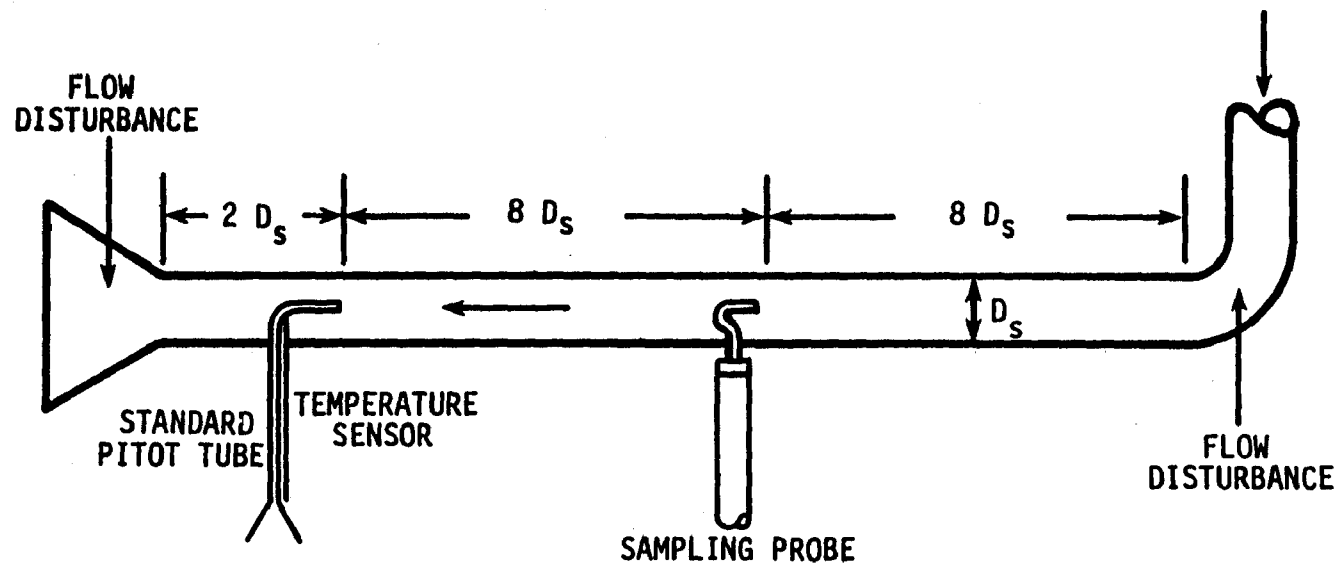
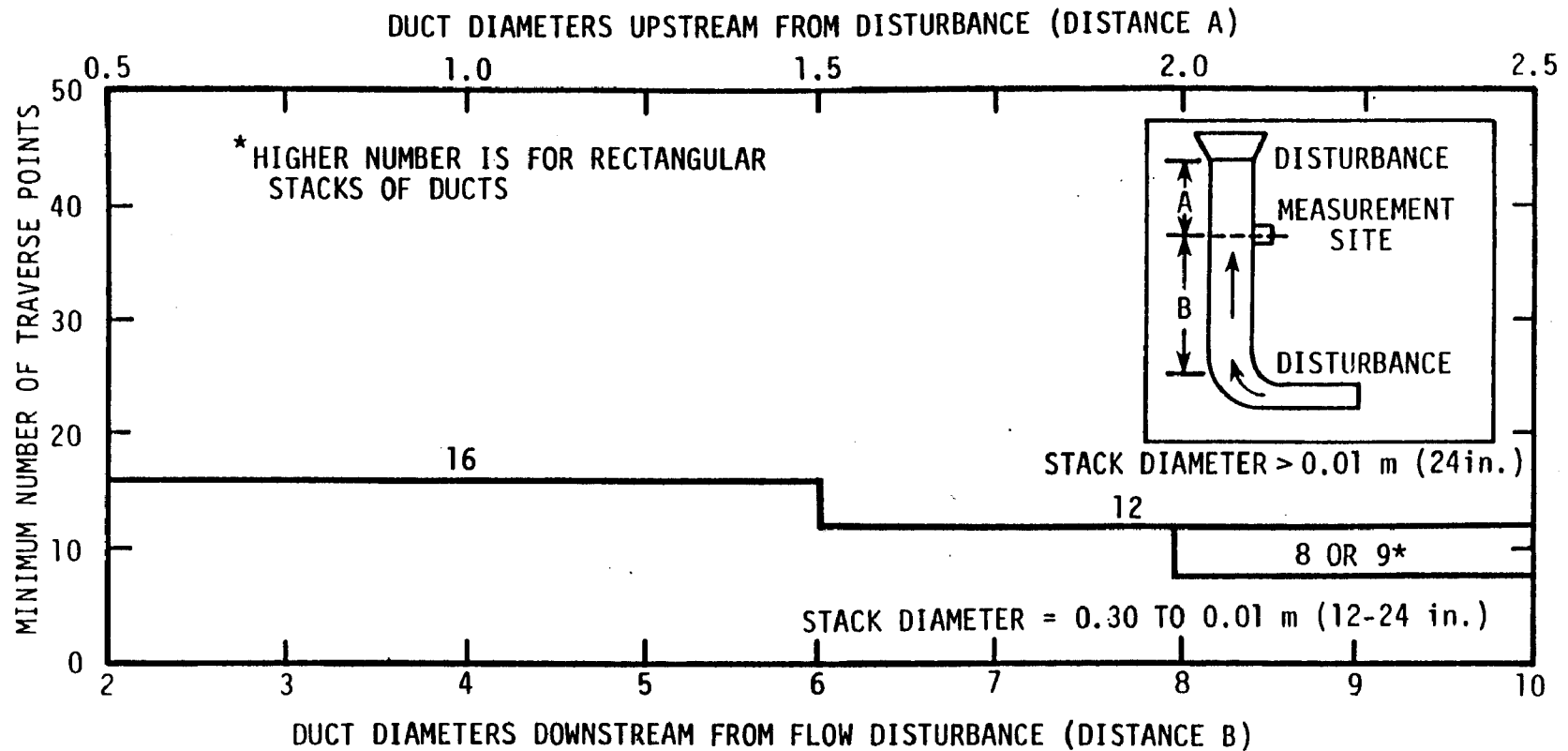
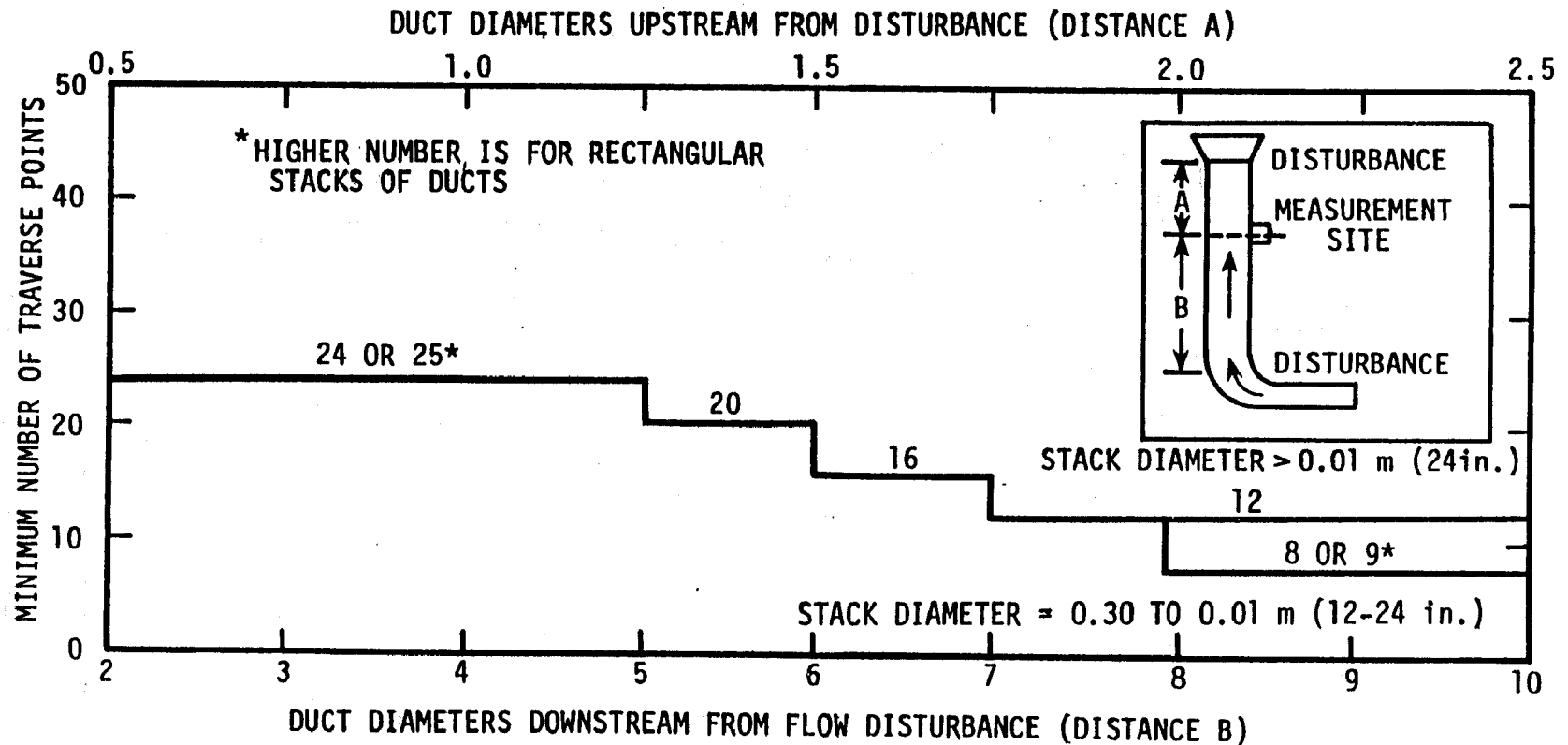


Figure 1A-1.

# MINIMUM NUMBER OF TRAVERSE POINTS FOR VELOCITY (NONPARTICULATE) TRAVERSE



# MINIMUM NUMBER OF TRAVERSE POINTS FOR PARTICULATE TRAVERSE



(Sec. 114 of the Clean Air Act as amended (42 U.S.C. 7414))

It is proposed that Appendix A of 40 CFR Part 60 be amended as follows:

2. Reference Method 1A is added to Appendix A as follows:

**Appendix A—Reference Methods**

\* \* \* \* \*

**Method 1A—Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts**

**1. Applicability and Principle**

The applicability and principle of this method are identical to Method 1, except its applicability is limited to stacks or ducts less than about 0.30 meter (12 in.) in diameter, or  $0.071 \text{ m}^2$  (113 in.<sup>2</sup>) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter, or  $0.0081 \text{ m}^2$  (12.57 in.<sup>2</sup>) in cross-sectional area.

In these small diameter stacks or ducts the conventional pitot assembly (consisting of a Type S pitot tube attached to a sampling probe, equipped with a nozzle and thermocouple) blocks a significant cross-section of the duct and prevents a true traverse. Therefore, for particulate sampling in small stacks or ducts, the gas velocity is measured using a standard pitot tube downstream of the actual emission testing site. The straight run of duct between the sampling and velocity measurement sites allows the flow profile, temporarily disturbed by the presence of the sampling probe, to redevelop and stabilize.

The cross-sectional layout and location of traverse points and the verification of the absence of cyclonic flow are the same as in Method 1, Sections 2.3 and 2.4, respectively. Differences from Method 1, except as noted, are given below.

**2. Procedure**

**2.1 Selection of Measurement Site.**

**2.1.1 Particulate Measurements—Steady or Unsteady Flow.** Select a particulate measurement site located preferably at least eight equivalent stack or duct diameters downstream and 10 equivalent diameters upstream from any flow disturbances such as a bends, expansions, or contractions in the stack, or from a visible flame. Next, locate the velocity measurement site eight equivalent diameters downstream of the particulate measurement site. See Figure 1A-1. If such locations are not available, select an alternative particulate measurement location at least two equivalent stack or duct diameters downstream and two and one-half diameters upstream from any flow disturbance. Then, locate the velocity measurement site two equivalent diameters downstream from the particulate measurement site. (See Section 2.1 of Method 1 for calculating equivalent diameters for a rectangular cross-section.)



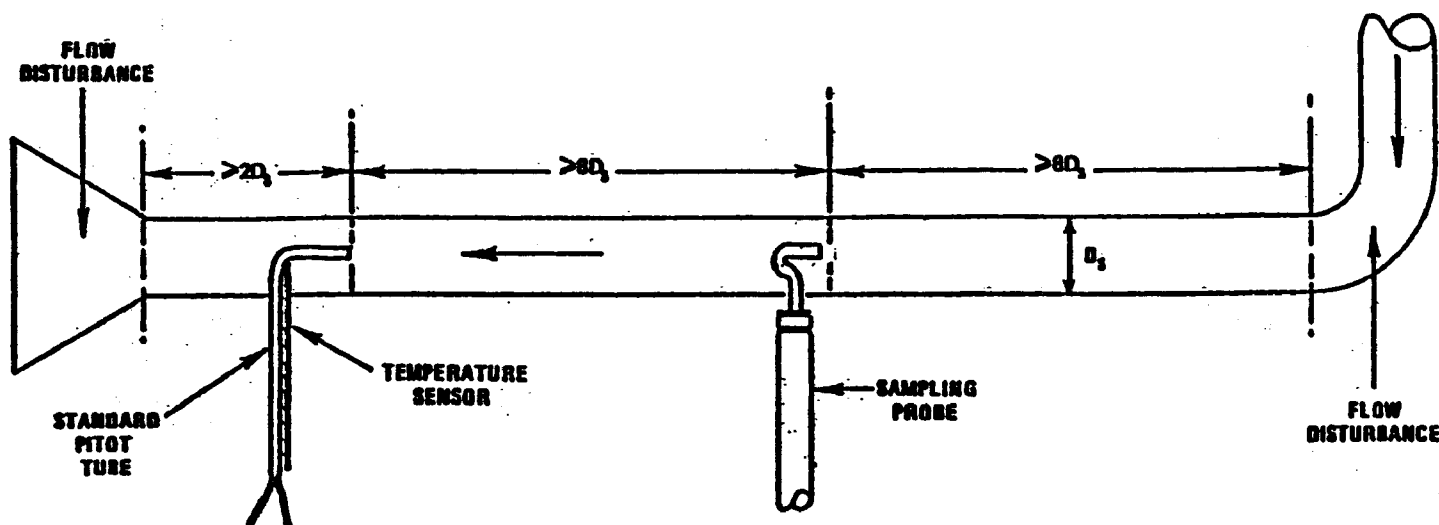


Figure 1A-1. Recommended sampling arrangement for small ducts.

**2.1.2 Particulate (Steady Flow) or Velocity (Steady or Unsteady Flow) Measurements.** If the average total volumetric flow rate in a duct is constant with respect to time or if only velocity measurements are required use the same criterion as in Section 2.1 of Method 1.

**2.2. Determining the Number of Traverse Points.**

**2.2.1 Particulate Measurements (Steady or Unsteady Flow).** Use Figure 1-1 of Method 1 to determine the number of traverse points. Before referring to the figure, however, determine the distance between the velocity and sampling sites and the distances to the nearest upstream and downstream disturbances and divide each distance by the stack diameter or equivalent diameter to determine the distances in terms of the number of duct diameters. Then, determine the number of traverse points from Figure 1-1 of Method 1 corresponding to each of these three distances. Choose the highest of the three numbers of traverse points (or a greater number) so that for circular ducts the number is a multiple of four; for rectangular ducts use one of those numbers shown in Table 1.1 of Method 1.

**2.2.2 Particulate (Steady Flow) and Velocity (Non-Particulate) Measurements.** Use Figure 1A-3 to determine number of traverse points, following the same procedure used for particulate traverses as described in Section 2.2.1 of Method 1.

### 3. Bibliography

1. Same as Method 1, Section 3, Citations 1 through 6.
2. Vollaro, Robert F. Recommended Procedure for Sample Traverses in Ducts Smaller Than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, North Carolina. January 1977.

METHOD 2A. DIRECT MEASUREMENT OF GAS VOLUME  
THROUGH PIPES AND SMALL DUCTS

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of gas flow rates in pipes and small ducts, either in-line or at exhaust positions, within the temperature range of 0 to 50°C.

1.2 Principle. A gas volume meter is used to directly measure gas volume. Temperature and pressure measurements are made to correct the volume to standard conditions.

2. Apparatus

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

2.1 Gas Volume Meter. A positive displacement meter, turbine meter, or other direct volume measuring device capable of measuring volume to within 2 percent. The meter shall be equipped with a temperature gauge ( $\pm 2$  percent of the minimum absolute temperature) and a pressure gauge ( $\pm 2.5$  mm Hg). The manufacturer's recommended capacity of the meter shall be sufficient for the expected maximum and minimum flow rates at the sampling conditions. Temperature, pressure, corrosive characteristics, and pipe size are factors necessary to consider in choosing a suitable gas meter.

2.2 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg. In many cases,

the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested, and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg per 30-meter elevation increase, or vice-versa for elevation decrease.

2.3 Stopwatch. Capable of measurement to within 1 second.

### 3. Procedure

3.1 Installation. As there are numerous types of pipes and small ducts that may be subject to volume measurement, it would be difficult to describe all possible installation schemes. In general, flange fittings should be used for all connections wherever possible. Gaskets or other seal materials should be used to assure leak-tight connections. The volume meter should be located so as to avoid severe vibrations and other factors that may affect the meter calibration.

3.2 Leak Test. A volume meter installed at a location under positive pressure may be leak-checked at the meter connections by using a liquid leak detector solution containing a surfactant. Apply a small amount of the solution to the connections. If a leak exists, bubbles will form, and the leak must be corrected.

A volume meter installed at a location under negative pressure is very difficult to test for leaks without blocking flow at the inlet of the line and watching for meter movement. If this procedure is not possible, visually check all connections and assure tight seals.

### 3.3 Volume Measurement.

3.3.1 For sources with continuous, steady emission flow rates, record the initial meter volume reading, meter temperature(s), meter pressure, and start the stopwatch. Throughout the test period, record the meter temperature(s) and pressure so that average values can be determined. At the end of the test, stop the timer and record the elapsed time, the final volume reading, meter temperature(s), and pressure. Record the barometric pressure at the beginning and end of the test run. Record the data on a table similar to Figure 2A-1.

3.3.2 For sources with noncontinuous, non-steady emission flow rates, use the procedure in 3.3.1 with the addition of the following. Record all the meter parameters and the start and stop times corresponding to each process cyclical or noncontinuous event.

## 4. Calibration

4.1 Volume Meter. The volume meter is calibrated against a standard reference meter prior to its initial use in the field. The reference meter is a spirometer or liquid displacement meter with a capacity consistent with that of the test meter. Alternative references may be used upon approval of the Administrator.

Set up the test meter in a configuration similar to that used in the field installation (i.e., in relation to the flow moving device). Connect the temperature and pressure gauges as they are to be used in the field. Connect the reference meter at the inlet of the flow line, if appropriate for the meter, and begin gas flow through the system to condition the meters. During this conditioning operation, check the system for leaks.

Plant \_\_\_\_\_  
 Date \_\_\_\_\_ Run Number \_\_\_\_\_  
 Sample Location \_\_\_\_\_  
 Barometric Pressure mm Hg \_\_\_\_\_ Start \_\_\_\_\_ Finish \_\_\_\_\_  
 Operators \_\_\_\_\_  
 Meter Number \_\_\_\_\_ Meter Calibration Coefficient \_\_\_\_\_  
 Last Date Calibrated \_\_\_\_\_

Time	Volume	Static	Temperature		
Run/clock	Meter reading	pressure mm Hg			
Average					

Figure 2A-1. Volume flow rate measurement data.

The calibration shall be run over at least three different flow rates. The calibration flow rates shall be about 0.3, 0.6, and 0.9 times the meter's rated maximum flow rate.

For each calibration run, the data to be collected include: reference meter initial and final volume readings, the test meter initial and final volume reading, meter average temperature and pressure, barometric pressure, and run time. Repeat the runs at each flow rate at least three times.

Calculate the test meter calibration coefficient,  $Y_m$ , for each run as follows:

$$Y_m = \frac{(V_{rf} - V_{ri})(t_r + 273)}{(V_{mf} - V_{mi})(t_m + 273)} \frac{P_b}{(P_b + P_g)} \quad \text{Eq. 2A-1}$$

Where:

$Y_m$  = Test volume meter calibration coefficient, dimensionless.

$V_r$  = Reference meter volume reading,  $m^3$ .

$V_m$  = Test meter volume reading,  $m^3$ .

$t_r$  = Reference meter average temperature,  $^{\circ}C$ .

$t_m$  = Test meter average temperature,  $^{\circ}C$ .

$P_b$  = Barometric pressure, mm Hg.

$P_g$  = Test meter average static pressure, mm Hg.

f = Final reading for run.

i = Initial reading for run.

Compare the three  $Y_m$  values at each of the flow rates tested and determine the maximum and minimum values. The difference between

the maximum and minimum values at each flow rate should be no greater than 0.030. Extra runs may be required to complete this requirement. If this specification cannot be met in six successive runs, the test meter is not suitable for use. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications are met at all the flow rates, average all the  $Y_m$  values for an average meter calibration coefficient,  $\bar{Y}_m$ .

The procedure above shall be performed at least once for each volume meter. Therefore, an abbreviated calibration check shall be completed after each field test. The calibration of the volume meter shall be checked by performing three calibration runs at a single, intermediate flow rate (based on the previous field test) with the meter pressure set at the average value encountered in the field test. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of flow as described above. Note: If the volume meter calibration coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the greater value of pollutant emission rate.

4.2 Temperature Gauge. After each test series, check the temperature gauge at ambient temperature. Use an ASTM mercury-in-glass reference thermometer, or equivalent, as a reference. If the gauge being checked agrees within 2 percent (absolute temperature) of the reference, the temperature data collected in the field shall be considered valid. Otherwise, the test data shall be considered

invalid or adjustments of the test results shall be made, subject to the approval of the Administrator.

4.3 Barometer. Calibrate the barometer used against a mercury barometer prior to the field test.

## 5. Calculations

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

### 5.1 Nomenclature

$P_b$  = Barometric pressure, mm Hg.

$P_g$  = Average static pressure in volume meter, mm Hg.

$Q_s$  = Gas flow rate,  $m^3/min$ , standard conditions.

$T_m$  = Average absolute meter temperature, °K.

$V_m$  = Meter volume reading,  $m^3$ .

$\bar{Y}_m$  = Meter calibration coefficient, dimensionless.

$f$  = Final reading for run.

$i$  = Initial reading for run.

$s$  = Standard conditions, 20° C and 760 mm Hg.

$\theta$  = Elapsed run time, min.



## 5.2 Volume.

$$V_{ms} = 0.3853 \bar{V}_m (V_{mf} - V_{mi}) \left( \frac{P_b + P_g}{T_m} \right) \quad \text{Eq. 2A-2}$$

## 5.3 Gas Flow Rate.

$$Q_s = \frac{V_{ms}}{\theta} \quad \text{Eq. 2A-3}$$

## 6. References

6.1 United States Environmental Protection Agency. Standards of Performance for New Stationary Sources, Revisions to Methods 1-8. Title 40, part 60. Washington, D.C. Federal Register Vol. 42, No. 160. August 18, 1977.

6.2 Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. APTD-0576. March 1972.

6.3 Wortman, Martin, R. Vollaro, and P.R. Westlin. Dry Gas Volume Meter Calibrations. Source Evaluation Society Newsletter. Vol. 2, No. 2. May 1977.

6.4 Westlin, P.R. and R.T. Shigehara. Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration Standards. Source Evaluation Society Newsletter. Vol. 3, No. 1. February 1978.

**Method 2A. Direct Measurement of Gas Volume Through Pipes and Small Ducts****1. Applicability and Principle.**

**1.1 Applicability.** This method applies to the measurement of gas flow rates in pipes and small ducts, either in-line or at exhaust positions, within the temperature range of 0 to 50°C.

**1.2 Principle.** A gas volume meter is used to measure gas volume directly. Temperature and pressure measurements are made to correct the volume to standard conditions.

**2. Apparatus.**

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

**2.1 Gas Volume Meter.** A positive displacement meter, turbine meter, or other direct volume measuring device capable of measuring volume to within 2 percent. The meter shall be equipped with a temperature gauge ( $\pm$  percent of the minimum absolute temperature) and a pressure gauge ( $\pm 2.5$  mm Hg). The manufacturer's recommended capacity of the meter shall be sufficient for the expected maximum and minimum flow rates at the sampling conditions. Temperature, pressure, corrosive characteristics, and pipe size are factors necessary to consider in choosing a suitable gas meter.

**2.2 Barometer.** A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg. In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested, and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg per 30-meter elevation increase, or vice-versa for elevation decrease.

**2.3 Stopwatch.** Capable of measurement to within 1 second.

**3. Procedure.**

**3.1 Installation.** As there are numerous types of pipes and small ducts that may be subject to volume measurement, it would be difficult to describe all possible installation schemes. In general, flange fittings should be used for all connections wherever possible. Gaskets or other seal materials should be used to assure leak-tight connections. The volume meter should be located so as to avoid severe vibrations and other factors that may affect the meter calibration.

**3.2 Leak Test.** A volume meter installed at a location under positive pressure may be leak-checked at the meter connections by using a liquid leak detector solution containing a surfactant. Apply a small amount of the solution to the connections. If a leak exists, bubbles will form, and the leak must be corrected.

A volume meter installed at a location under negative pressure is very difficult to test for leaks without blocking flow at the inlet of the line and watching for meter movement. If this procedure is not possible, visually check all connections and assure tight seals.

**3.3 Volume Measurement.**

**3.3.1** For sources with continuous, steady emission flow rates, record the initial meter volume reading, meter temperature(s), meter pressure, and start the stopwatch. Throughout the test period, record the meter temperature(s) and pressure so that average values can be determined. At the end of the test, stop the timer and record the elapsed time, the final volume reading, meter temperature(s), and pressure. Record the barometric pressure at the beginning and end of the test run. Record the data on a table similar to Figure 2A-1.

**BILLING CODE 6580-60-M**

**3.3.2** For sources with noncontinuous, non-steady emission flow rates, use the procedure in 3.3.1 with the addition of the following: Record all the meter parameters and the start and stop times corresponding to each process cyclical or noncontinuous event.

**4. Calibration.**

**4.1 Volume Meter.** The volume meter is calibrated against a standard reference meter prior to its initial use in the field. The reference meter is a spirometer or liquid displacement meter with a capacity consistent with that of the test meter.

Alternately, a calibrated, standard pitot may be used as the reference meter in conjunction with a wind-tunnel assembly. Attach the test meter to the wind tunnel so that the total flow passes through the test meter. For each calibration run, conduct a 4-point traverse along one stack diameter at a position at least eight diameters of straight tunnel downstream and two diameters upstream of any bend, inlet, or air mover. Determine the traverse point locations as specified in Method 1. Calculate the reference volume using the velocity values following the procedure in Method 2, the wind tunnel cross-sectional area, and the run time.

Set up the test meter in a configuration similar to that used in the field installation (i.e., in relation to the flow moving device). Connect the temperature and pressure gauges as they are to be used in the field. Connect the reference meter at the inlet of the flow line, if appropriate for the meter, and begin gas flow through the system to condition the meters. During this conditioning operation, check the system for leaks.

The calibration shall be run over at least three different flow rates. The calibration flow rates shall be about 0.3, 0.6, and 0.9 times the test meter's rated maximum flow rate.

For each calibration run, the data to be collected include: reference meter initial and final volume readings, the test meter initial and final volume reading, meter average temperature and pressure, barometric pressure, and run time. Repeat the runs at each flow rate at least three times.

Calculate the test meter calibration coefficient,  $Y_m$ , for each run as follows:

$$Y_m = \frac{(V_r - V_m)(t_r + 273)}{(V_m - V_m)(t_m + 273)} \frac{P_b}{(P_b + P_s)}$$

**Eq. 2A-1**

$Y_m$  = Test volume meter calibration coefficient, dimensionless.

$V_r$  = Reference meter volume reading,  $m^3$ .

$V_m$  = Test meter volume reading,  $m^3$ .

$t_r$  = Reference meter average temperature, °C.

$t_m$  = Test meter average temperature, °C.

$P_b$  = Barometric pressure, mm Hg.

$P_s$  = Test meter average static pressure, mm Hg.

$f$  = Final reading for run.

$i$  = Initial reading for run.

Compare the three  $Y_m$  values at each of the flow rates tested and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra runs may be required to complete this requirement. If this specification cannot be met in six successive runs, the test meter is not suitable for use. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications are met at all the flow rates, average all the  $Y_m$  values from runs meeting the specifications to obtain an average meter calibration coefficient,  $Y_m$ .

The procedure above shall be performed at least once for each volume meter. Thereafter, an abbreviated calibration check shall be completed following each field test. The calibration of the volume meter shall be checked by performing three calibration runs at a single, intermediate flow rate (based on the previous field test) with the meter pressure set at the average value encountered in the field test. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of flow as described above.

**Note.**—If the volume meter calibration coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the greater value of pollutant emission rate.

Plant \_\_\_\_\_

Date \_\_\_\_\_ Run Number \_\_\_\_\_

Sample Location \_\_\_\_\_

Barometric Pressure mm Hg Start \_\_\_\_\_ Finish \_\_\_\_\_

Operators \_\_\_\_\_

Meter Number \_\_\_\_\_ Meter Calibration Coefficient \_\_\_\_\_

Last Date Calibrated \_\_\_\_\_

Time	Volume	Static	Temperature	
Run/clock	Meter reading	pressure mm Hg		
			°C	°K
Average				

Figure 2A-1. Volume flow rate measurement data.

**4.2 Temperature Gauge.** After each test series, check the temperature gauge at ambient temperature. Use an American Society for Testing and Materials (ASTM) mercury-in-glass reference thermometer, or equivalent, as a reference. If the gauge being checked agrees within 2 percent (absolute temperature) of the reference, the temperature data collected in the field shall be considered valid. Otherwise, the test data shall be considered invalid or adjustments of the test results shall be made, subject to the approval of the Administrator.

**4.3 Barometer.** Calibrate the barometer used against a mercury barometer prior to the field test.

**5. Calculations.**

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

**5.1 Nomenclature**

$P_b$  = Barometric pressure, mm Hg.

$P_s$  = Average static pressure in volume meter, mm Hg.

$Q_s$  = Gas flow rate,  $m^3/min$ , standard conditions.

$T_m$  = Average absolute meter temperature, °K.

$V_m$  = Meter volume reading,  $m^3$ .

$Y_m$  = Average meter calibration coefficient, dimensionless.

$f$  = Final reading for test period.

$i$  = Initial reading for test period.

$s$  = Standard conditions, 20° C and 760 mm Hg.

$\Theta$  = Elapsed test period time, min.

**5.2 Volume.**

$$V_m = 0.3853 Y_m (V_m - V_m) \frac{(P_b + P_s)}{T_m}$$

Eq. 2A-2

**5.3 Gas Flow Rate.**

$$Q_s = \frac{V_m}{\Theta}$$

Eq. 2A-3

**6. Bibliography.**

**6.1** Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. APTD-0578. March 1972.

**6.2** Wortman, Martin, R. Vollaro, and P.R. Westlin. Dry Gas Volume Meter Calibrations. Source Evaluation Society Newsletter. Vol. 2, No. 2. May 1977.

**6.3** Westlin, P.R. and R.T. Shigehara. Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration Standards. Source Evaluation Society Newsletter. Vol. 3, No. 1. February 1978.

## METHOD 2B - DETERMINATION OF EXHAUST GAS VOLUME

### FLOW RATE FROM GASOLINE VAPOR INCINERATORS

#### Applicability and Principle

1.1 Applicability. This method applies to the measurement of exhaust volume flow rate from incinerators that process gasoline vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). It is assumed that the amount of auxiliary fuel is negligible.

1.2 Principle. The incinerator exhaust flow rate is determined by carbon balance. Organic carbon concentration and volume flow rate are measured at the incinerator inlet. Organic carbon, carbon dioxide ( $\text{CO}_2$ ), and carbon monoxide ( $\text{CO}$ ) concentrations are measured at the outlet. Then the ratio of total carbon at the incinerator inlet and outlet is multiplied by the inlet volume to determine the exhaust volume and volume flow rate.

#### 2. Apparatus

2.1 Volume Meter. Equipment described in Method 2A.

2.2 Organic Analyzers (2). Equipment described in Method 25A or 25B.

2.3  $\text{CO}$  Analyzer. Equipment described in Method 10.

2.4  $\text{CO}_2$  Analyzer. A nondispersive infrared (NDIR)  $\text{CO}_2$  analyzer and supporting equipment with comparable specifications as  $\text{CO}$  analyzer described in Method 10.

### 3. Procedure

3.1 Inlet Installation. Install a volume meter in the vapor line to incinerator inlet according to the procedure in Method 2A. At the volume meter inlet, install a sample probe as described in Method 25A. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the vapor line cross-section. Connect to the probe a leak-tight, heated (if necessary to prevent condensation) sample line (stainless steel or equivalent) and an organic analyzer system as described in Method 25A or 25B.

3.2 Exhaust Installation. Three sample analyzers are required for the incinerator exhaust - CO<sub>2</sub>, CO, and organic. A sample manifold with a single sample probe may be used. Install a sample probe as described Method 25A or, alternatively, a single opening probe positioned so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section. Connect a leak-tight heated sample line to the sample probe. Heat the sample line sufficiently to prevent any condensation.

3.3 Recording Requirements. The output of each analyzer must be permanently recorded on an analog strip chart, digital recorder, or other recording device. The chart speed or number of readings per time unit must be similar for all analyzers so that data can be correlated. The minimum data recording requirement for each analyzer is one measurement value per minute during the incinerator test period.

3.4 Preparation. Prepare and calibrate all equipment and analyzers according to the procedures in the respective methods. All calibration gases must be introduced at the connection between the probe and the sample line. If a manifold system is used for the

exhaust analyzers, all the analyzers and sample pumps must be operating when the calibrations are done. Note: For the purposes of this test, methane should not be used as an organic calibration gas.

3.5 Sampling. At the beginning of the test period, record the initial parameters for the inlet volume meter according to the procedures in Method 2A and mark all of the recorder strip charts to indicate the start of the test. Continue recording inlet organic and exhaust CO<sub>2</sub>, CO, and organic concentrations throughout the test. During periods of process interruption and halting of gas flow, stop the timer and mark the recorder strip charts so that data from this interruption are not included in the calculations. At the end of the test period, record the final parameters for the inlet volume meter and mark the end on all of the recorder strip charts.

3.6 Post Test Calibrations. At the conclusion of the sampling period, introduce the calibration gases as specified in the respective reference methods. If analyzer output does not meet the specifications of the method, invalidate the test data for that period. Alternatively, calculate the volume results using initial calibration data and using final calibration data and report both resulting volumes. Then, for emissions calculations, use the volume measurement resulting in the greatest emission rate or concentration.

#### 4. Calculations

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

#### 4.1 Nomenclature

- $CO_e$  - Mean carbon monoxide concentration in system exhaust, ppmv.
- $CO_{2e}$  - Mean carbon dioxide concentration in system exhaust, ppmv.
- $HC_e$  - Mean organic concentration in system exhaust as defined by the calibration gas, ppmv.
- $HC_i$  - Mean organic concentration in system inlet as defined by the calibration gas, ppmv.
- $K$  - Calibration gas factor = 2 for ethane calibration gas.  
= 3 for propane calibration gas.  
= 4 for butane calibration gas.
- $V_{es}$  - Exhaust gas volume,  $m^3$ .
- $V_{is}$  - Inlet gas volume,  $m^3$ .
- $Q_{es}$  - Exhaust gas volume flow rate,  $m^3/min$ .
- $Q_{is}$  - Inlet gas volume flow rate,  $m^3/min$ .
- $\theta$  - Sample run time, min.
- $s$  - Standard Conditions: 20°C, 760 mm Hg.
- 300 - Estimated concentration of ambient  $CO_2$ , ppmv.  
( $CO_2$  concentration in the ambient air may be measured during the test period using an NDIR and the mean value substituted into the equation.)

4.2 Concentrations. Determine mean concentrations of inlet organics, outlet  $CO_2$ , CO, and outlet organics according to the procedures in the respective methods and the analyzers' calibration curves, and for the time intervals specified in the applicable regulations.



Concentrations should be determined on a parts per million by volume (ppmv) basis.

4.3 Exhaust Gas Volume. Calculate the exhaust gas volume as follows:

$$V_{es} = V_{is} \frac{K(HC_i)}{K(HC_e) + CO_{2e} + CO_e - 300} \quad \text{Eq. 2B-1}$$

4.4 Exhaust Gas Volume Flow Rate. Calculate the exhaust gas volume flow rate as follows:

$$Q_{es} = \frac{V_{es}}{\theta} \quad \text{Eq. 2B-2}$$

## 5. References

5.1 Measurement of Volatile Organic Compounds. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711. Publication No. EPA-450/2-78-041. October 1978. p. 55.

5.2 Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Chapter 1, part 60, Appendix A. Washington, D.C. Office of the Federal Register. March 8, 1974.

5.3 Method 2A - Determination of Gas Flow Rate  
in Pipes and Small Ducts. Tentative Method. U.S. Environmental  
Protection Agency. Office of Air Quality Planning and Standards.  
Research Triangle Park, N.C. 27711. March 1980.

5.4 Method 25A - Determination of Total Gaseous  
Organic Compounds Using a Flame Ionization Analyzer. Tentative  
Method. U.S. Environmental Protection Agency. Office of Air  
Quality Planning and Standards. Research Triangle Park, N.C. 27711.  
March 1980.

5.5 Method 25B - Determination of Total Gaseous  
Organic Compounds Using a Nondispersive Infrared Analyzer.  
Tentative Method. U.S. Environmental Protection Agency. Office of  
Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.  
March 1980.

**Method 2B—Determination of Exhaust Gas Volume Flow Rate From Gasoline Vapor Incinerators****Applicability and Principle**

**1.1 Applicability.** This method applies to the measurement of exhaust volume flow rate from incinerators that process gasoline vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). It is assumed that the amount of auxiliary fuel is negligible.

**1.2 Principle.** The incinerator exhaust flow rate is determined by carbon balance. Organic carbon concentration and volume flow rate are measured at the incinerator inlet. Organic carbon, carbon dioxide (CO<sub>2</sub>), and carbon monoxide (CO) concentrations are measured at the outlet. Then the ratio of total carbon at the incinerator inlet and outlet is multiplied by the inlet volume to determine the exhaust volume and volume flow rate.

**2. Apparatus.**

**2.1 Volume Meter.** Equipment described in Method 2A.

**2.2 Organic Analyzer (2).** Equipment described in Method 25A or 25B.

**2.3 CO Analyzer.** Equipment described in Method 10.

**2.4 CO<sub>2</sub> Analyzer.** A nondispersive infrared (NDIR) CO<sub>2</sub> analyzer and supporting equipment with comparable specifications as CO analyzer described in Method 10.

**3. Procedure.**

**3.1 Inlet Installation.** Install a volume meter in the vapor line to incinerator inlet according to the procedure in Method 2A. At the volume meter inlet, install a sample probe as described in Method 25A. Connect to the probe a leak-tight, heated (if necessary to prevent condensation) sample line (Stainless steel or equivalent) and an organic analyzer system as described in Method 25A or 25B.

**3.2 Exhaust Installation.** Three sample analyzers are required for the incinerator exhaust: CO<sub>2</sub>, CO, and organic analyzers. A sample manifold with a single sample probe may be used. Install a sample probe as described Method 25A. Connect a leak-tight heated sample line to the sample probe. Heat the sample line sufficiently to prevent any condensation.

**3.3 Recording Requirements.** The output of each analyzer must be permanently recorded on an analog strip chart, digital recorder, or other recording device. The chart speed or number of readings per time unit

must be similar for all analyzers so that data can be correlated. The minimum data recording requirement for each analyzer is one measurement value per minute.

**3.4 Preparation.** Prepare and calibrate all equipment and analyzers according to the procedures in the respective methods. For the CO<sub>2</sub> analyzer, follow the procedures described in Method 10 for CO analysis substituting CO<sub>2</sub> calibration gas where the method calls for CO calibration gas. The span value for the CO<sub>2</sub> analyzer shall be 15 percent by volume. All calibration gases must be introduced at the connection between the probe and the sample line. If a manifold system is used for the exhaust analyzers, all the analyzers and sample pumps must be operating when the calibrations are done. Note: For the purposes of this test, methane should not be used as an organic calibration gas.

**3.5 Sampling.** At the beginning of the test period, record the initial parameters for the inlet volume meter according to the procedures in Method 2A and mark all of the recorder strip charts to indicate the start of the test. Continue recording inlet organic and exhaust CO<sub>2</sub>, CO, and organic concentrations throughout the test. During periods of process interruption and halting of gas flow, stop the timer and mark the recorder strip charts so that data from this interruption are not included in the calculations. At the end of the test period, record the final parameters for the inlet volume meter and mark the end on all of the recorder strip charts.

**3.6 Post Test Calibrations.** At the conclusion of the sampling period, introduce the calibration gases as specified in the respective reference methods. If an analyzer output does not meet the specifications of the method, invalidate the test data for the period. Alternatively, calculate the volume results using initial calibration data and using final calibration data and report both resulting volumes. Then, for emissions calculations, use the volume measurement resulting in the greatest emission rate or concentration.

**4. Calculations.**

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

**4.1 Nomenclature**

CO<sub>e</sub> = Mean carbon monoxide concentration in system exhaust, ppmv.

CO<sub>2e</sub> = Mean carbon dioxide concentration in system exhaust, ppmv.

HC<sub>e</sub> = Mean organic concentration in system exhaust as defined by the calibration gas, ppmv.

HC<sub>i</sub> = Mean organic concentration in system inlet as defined by the calibration gas, ppmv.

K = Calibration gas factor = 2 for ethane calibration gas.

= 3 for propane calibration gas.

= 4 for butane calibration gas.

= Appropriate response factor for other calibration gas.

V<sub>e</sub> = Exhaust gas volume, M<sup>3</sup>.

V<sub>i</sub> = Inlet gas volume, M<sup>3</sup>.

Q<sub>e</sub> = Exhaust gas volume flow rate, m<sup>3</sup>/min.

Q<sub>i</sub> = Inlet gas volume flow rate, m<sup>3</sup>/min.

e = Sample run time, min.

s = Standard Conditions: 20°C, 760 mm Hg.

300 = Estimated concentration of ambient

CO<sub>2</sub>, ppmv. (CO<sub>2</sub> concentration in the ambient air may be measured during the test period using an NDIR and the mean value substituted into the equation.)

**4.2 Concentrations.** Determine mean concentration of inlet organics, outlet CO<sub>2</sub>, outlet CO, and outlet organics according to the procedures in the respective methods and the analyzers' calibration curves, and for the time intervals specified in the applicable regulations. Concentrations should be determined on a parts per million by volume (ppmv) basis.

**4.3 Exhaust Gas Volume.** Calculate the exhaust gas volume as follows:

$$V_e = V_i \frac{K(HC_i)}{K(HC_e) + CO_{2e} - 300}$$

Eq. 2B-1

**4.4 Exhaust Gas Volume Flow Rate.**

Calculate the exhaust gas volume flow rate as follows:

$$Q_e = \frac{V_e}{e}$$

Eq. 2B-2

**5. Bibliography.**

5.1 Measurement of Volatile Organic Compounds. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711. Publication No. EPA-450/2-78-041. October 1978. p. 55.

\* \* \* \* \*

METHOD 2C - DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE  
FROM SMALL STACKS OR DUCTS (STANDARD PITOT TUBE)

1. Applicability and Principle

1.1 Applicability. The applicability of this method is identical to Method 2, except it is limited to stationary source stacks or ducts less than about 0.30 meter (12 in.) in diameter, or  $0.071 \text{ m}^2$  (113 in.<sup>2</sup>) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter, or  $0.0081 \text{ m}^2$  (12.57 in.<sup>2</sup>) in cross-sectional area.

The apparatus, procedure, calibration, calculations, and bibliography are the same as in Method 2, Sections 2, 3, 4, 5, and 6, except as noted in the following sections.

1.2 Principle. The average gas velocity in a stack or duct is determined from the gas density and from measurement of velocity heads with a standard pitot tube.

2. Apparatus

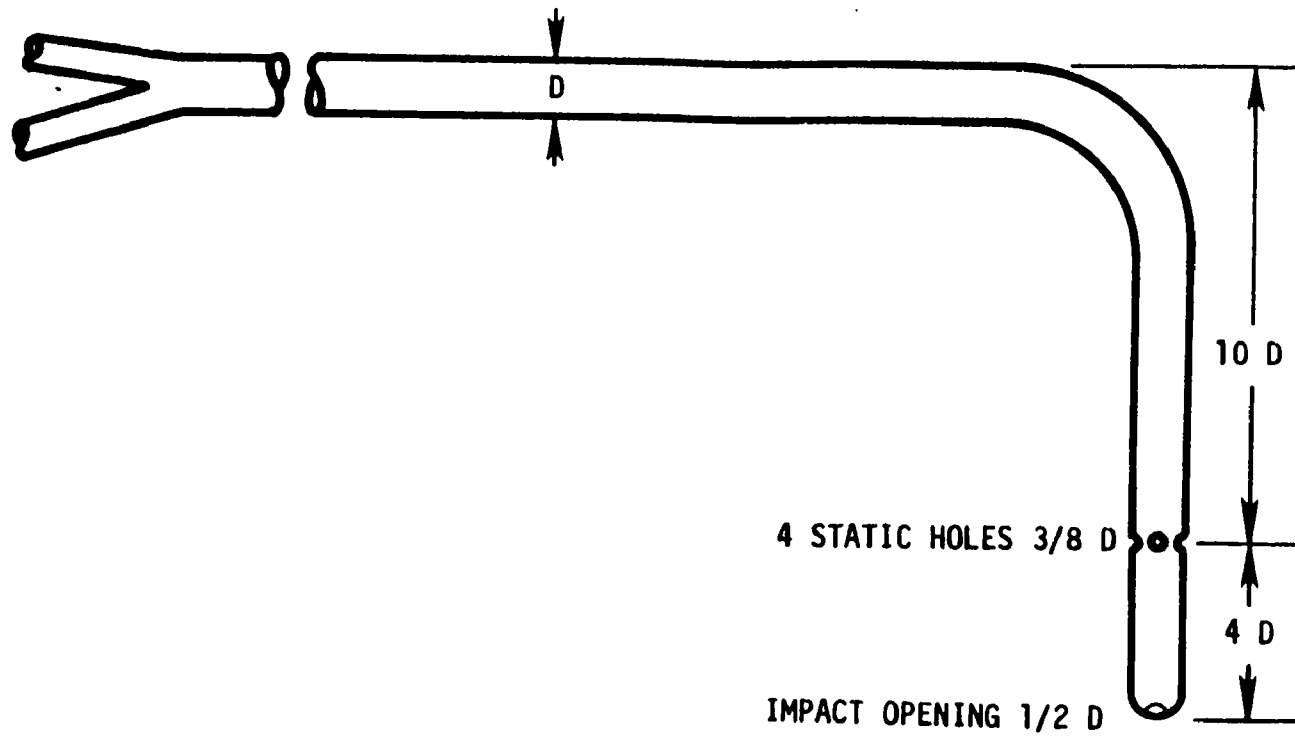
2.1 Standard Pitot Tube (instead of Type S). A standard pitot tube which meets the specifications of Section 2.7 of Method 2. Use a coefficient of 0.99 unless it is calibrated against another standard pitot tube with an NBS-traceable coefficient.

2.2 Alternative Pitot Tube. A modified hemispherical-nosed pitot tube (See Figure 2C-1), which features a shortened stem and enlarged impact and static pressure holes. Use a coefficient of 0.99 unless it is calibrated as mentioned in Section 2.1 above. This pitot tube is useful in particulate liquid droplet laden gas streams when a "back purge" is ineffective.

3. Procedure

Follow the general procedures in Section 3 of Method 2, except conduct

FIGURE 2C-1.

**MODIFIED HEMISPHERICAL-NOSED PITOT TUBE**

the measurements at the traverse points specified in Method 1A. The static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, the tester must furnish adequate proof that the openings of the pitot tube have not plugged during the traverse period; this can be done by taking the velocity head ( $\Delta p$ ) reading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another  $\Delta p$  reading. If the  $\Delta p$  readings made before and after the air purge are the same ( $\pm 5$  percent) the traverse is acceptable. Otherwise, reject the run. Note that if the  $\Delta p$  at the final traverse point is unsuitably low, another point may be selected. If "back-purging" at regular intervals is part of the procedure, then take comparative  $\Delta p$  readings, as above, for the last two back purges at which suitably high  $\Delta p$  readings are observed.

3. Reference Method 2C is added to Appendix A as follows:

**Appendix A—Reference Methods**

**Method 2C—Determination of Stack Gas Velocity and Volumetric Flow Rate From Small Stacks or Ducts (Standard Pitot Tube)**

**1. Applicability and Principle**

1.1 Applicability. The applicability of this method is identical to Method 2, except it is limited to stationary source stacks or ducts

less than about 0.30 meter (12 in.) in diameter, or  $0.071 \text{ m}^2$  (113 in.<sup>2</sup>) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter or  $0.0061 \text{ m}^2$  (12.57 in.<sup>2</sup>) in cross-sectional area.

The apparatus, procedure, calibration, calculations, and bibliography are the same as in Method 2, Sections 2, 3, 4, 5, and 6, except as noted in the following sections.

1.2 Principle. The average gas velocity in a stack or duct is determined from the gas density and from measurement of velocity heads with a standard pitot tube.

**2. Apparatus**

2.1 Standard Pitot Tube (instead of Type S). A standard pitot tube which meets the specifications of Section 2.7 of Method 2. Use a coefficient of 0.99 unless it is calibrated against another standard pitot tube with an NBS-traceable coefficient.

2.2 Alternative Pitot Tube. A modified hemispherical-nosed pitot tube (see Figure 2C-1), which features a shortened stem and enlarged impact and static pressure holes. Use a coefficient of 0.99 unless it is calibrated as mentioned in Section 2.1 above. This pitot tube is useful in particulate liquid droplet laden gas streams when a "back purge" is ineffective.

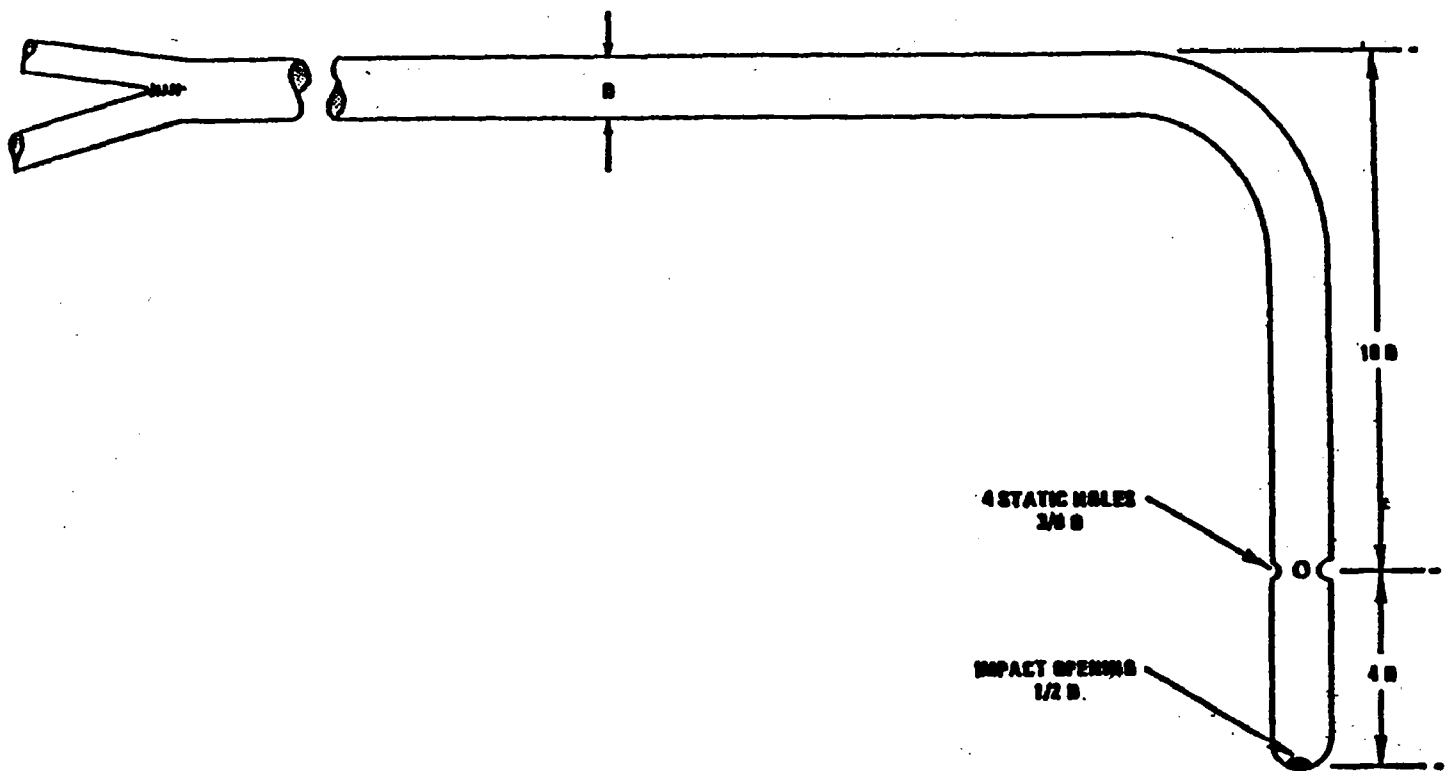


Figure 2C-1. Modified hemispherical-nosed pitot tube.

### 3. Procedure

Follow the general procedures in Section 3 of Method 2, except conduct the measurements at the traverse points specified in Method 1A. The static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, the tester must furnish adequate proof that the openings of the pitot tube have not plugged during the traverse period; this can be done by taking the velocity head ( $\Delta p$ ) heading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another  $\Delta p$  reading. If the  $\Delta$  readings made before and after the air purge are the same ( $\pm 5$  percent) the traverse is acceptable. Otherwise, reject the run. Note that if the  $\Delta p$  at the final traverse point is unsuitably low, another point may be selected. If "back purging" at regular intervals is part of the procedure, then take comparative  $\Delta p$  readings, as above, for the last two back purges at which suitably high  $\Delta p$  readings are observed.



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 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 chromatography 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.

### **5.1 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, amber-colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

5.1.11 Soap Film Flowmeter. 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  $\pm 2$  percent, for preparation 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 Chloroform.

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 chloroform. 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 550°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 50°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. Follow 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 on 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 determine 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 procedure 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. 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 sample to 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. Then use the low-concentration standard to verify the 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:

$$Q_2 = Q_1 \left[ \frac{P_2 T_1}{P_1 T_2} \right]^{\frac{1}{2}} \quad \text{Eq. 18-1}$$

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:

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

Where:

$C_a$  = Concentration of component "a" in ppm.

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

$q_a$  = Flow rate of 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:

$$C_a = 10^6 \bar{X} \left( \frac{q_{a1}}{q_{a1} + q_{d1}} \right) \left( \frac{q_{a2}}{q_{a2} + q_{d2}} \right) \quad \text{Eq. 18-3}$$

Where:

$C_a$  = Concentration of component "a" in ppm.

$\bar{X}_a$  = 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-capped 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:

$$C_{\text{std sol}} = \frac{760 (L_v) (\rho) (293 + T_m)}{293(M_f - M_i) (P_{\text{bar}} + P_m)} \quad \text{Eq. 18-4}$$

Where:

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

$L_v$  = Liquid volume injected, ml.

$\rho$  = Liquid density at room temperature, g/ml.

$T_m$  = Meter temperature, °C.

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

$P_{\text{bar}}$  = 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 attenuator 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, attenuator 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, 7.2, 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<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O), 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.** Follow 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 widget 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 is 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 for 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  $\pm 1$  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 within 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 record 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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**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<sub>2</sub>O, Data source \_\_\_\_\_

Moisture content \_\_\_\_\_ %, Data source \_\_\_\_\_

Particulate content \_\_\_\_\_, Data source \_\_\_\_\_

##### Gaseous components

N<sub>2</sub> \_\_\_\_\_ %

Hydrocarbons \_\_\_\_\_ ppm

O<sub>2</sub> \_\_\_\_\_ %

\_\_\_\_\_

CO \_\_\_\_\_ %

\_\_\_\_\_

CO<sub>2</sub> \_\_\_\_\_ %

\_\_\_\_\_

SO<sub>2</sub> \_\_\_\_\_ %

\_\_\_\_\_

##### 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.

<u>Components to be analyzed</u>	<u>Expected concentration</u>
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

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:

<u>Compound</u>	<u>Retention time</u>	<u>Attenuation</u>
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Figure 18-2. Chromatographic conditions data sheet.

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

	<u>Blank</u>	<u>Mixture 1</u>	<u>Mixture 2</u>	<u>Mixture 3</u>
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 <sup>2</sup> )	_____	_____	_____	_____
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 <sup>a</sup>	Flow rate (lab conditions) <sup>b</sup>
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____

<sup>a</sup> Vol. of gas may be measured in milliliters, liters or cubic feet.

<sup>b</sup> Convert to standard conditions (20° C and 760 mm Hg).

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

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

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

Figure 18-4. Rotameter calibration data sheet.



# SINGLE-STAGE CALIBRATION GAS DILUTION SYSTEM

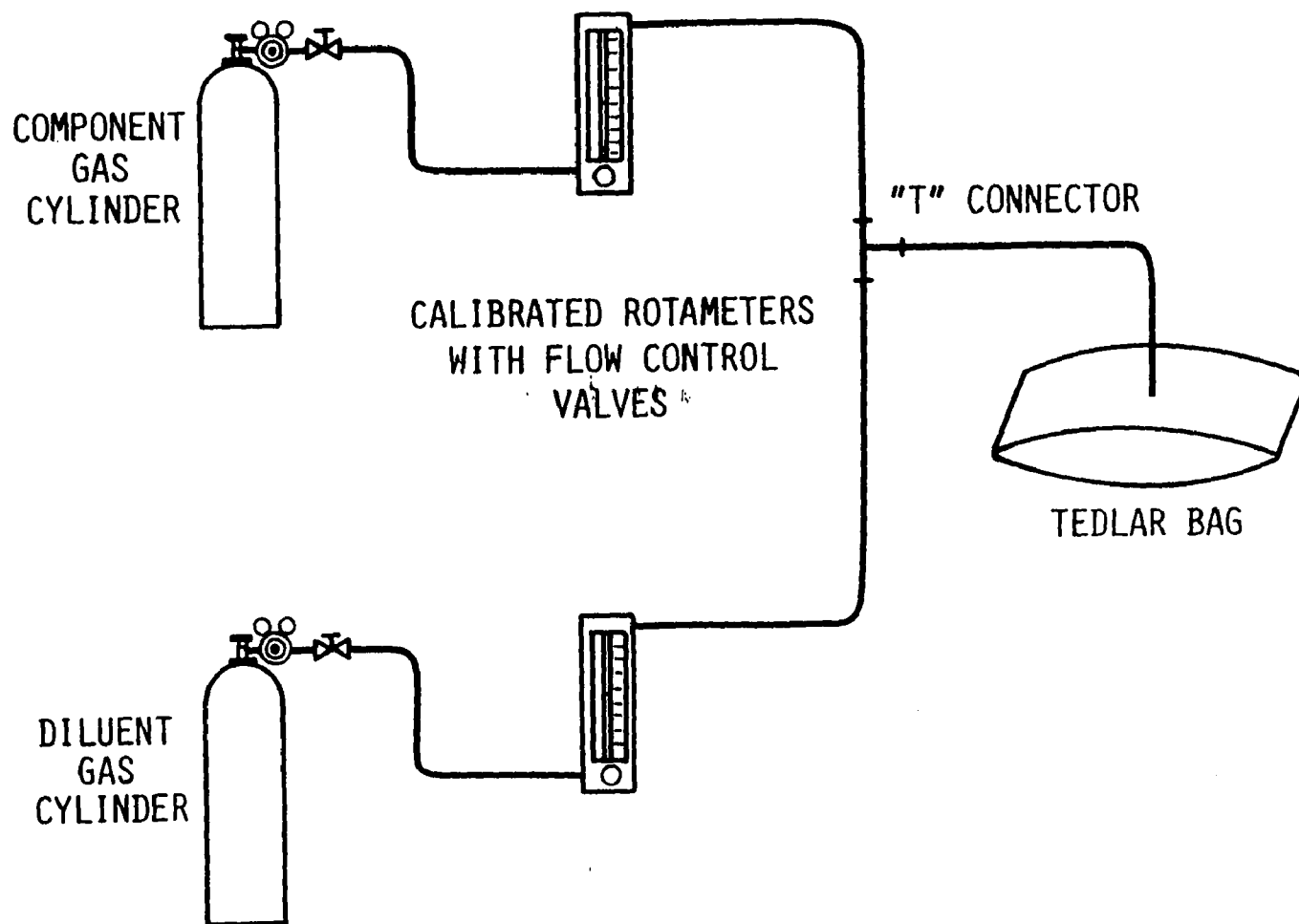


FIGURE 18-5.

# TWO-STAGE DILUTION APPARATUS

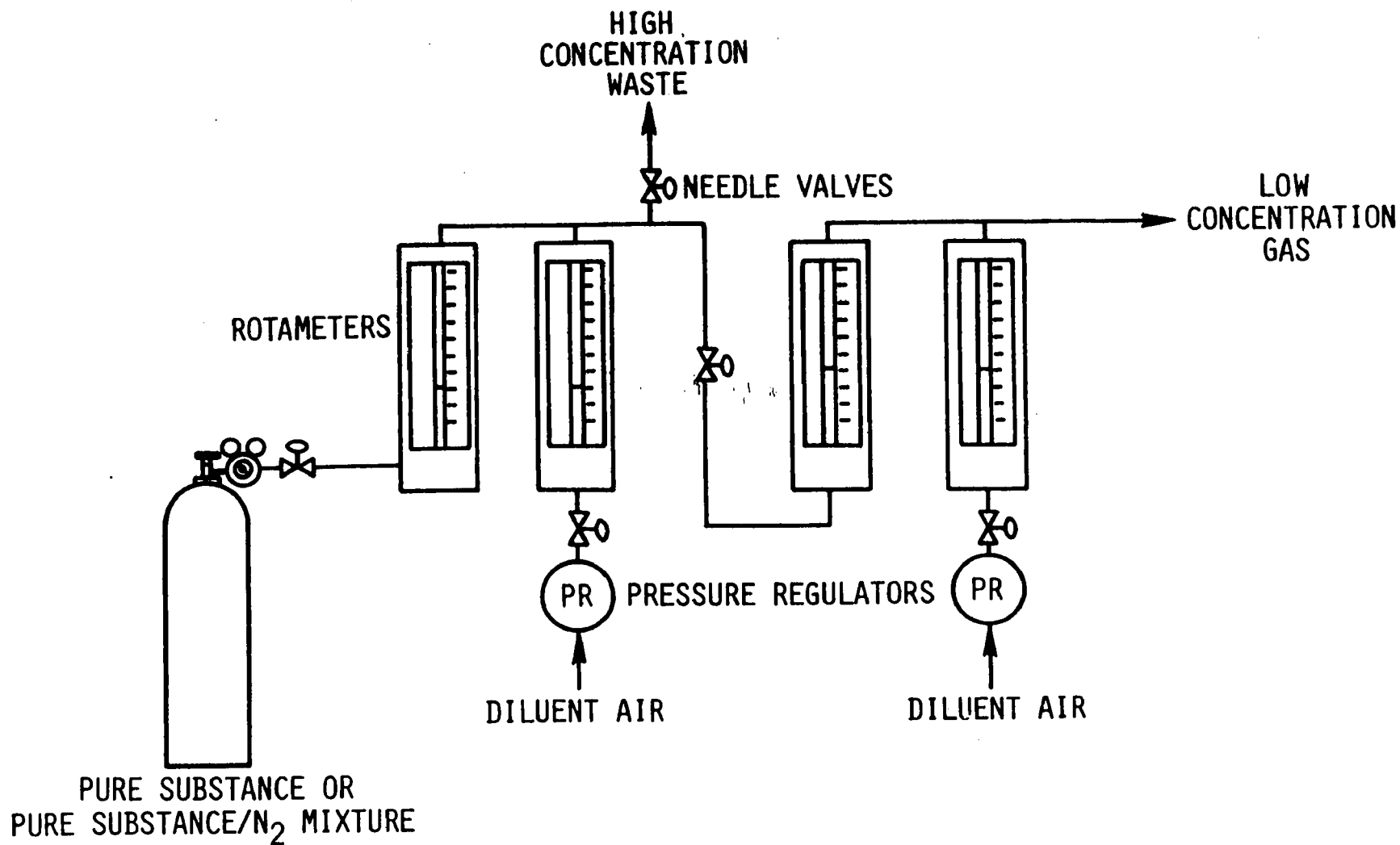


FIGURE 18-6.

1. High concentration as mixture

Component \_\_\_\_\_ Concentration \_\_\_\_\_ ppm  
 Diluent gas \_\_\_\_\_

2. Dilution and analysis at

Date \_\_\_\_\_

<u>Stage 1</u>	<u>Mixture 1</u>	<u>Mixture 2</u>	<u>Mixture 3</u>
Component gas-rotameter reading	_____	_____	_____
Diluent gas-rotameter reading	_____	_____	_____
Ambient temp. (°C)	_____	_____	_____
Manometer reading, inches H <sub>2</sub> O	_____	_____	_____
Flow rate component gas (ml/min)	_____	_____	_____
Flow rate diluent gas (ml/min)	_____	_____	_____
<u>Stage 2</u>			
Component gas-rotameter reading	_____	_____	_____
Diluent gas-rotameter reading	_____	_____	_____
Flow rate component gas (ml/min)	_____	_____	_____
Flow rate diluent gas (ml/min)	_____	_____	_____
Calculated concentration (ppm)	_____	_____	_____
<u>Analysis</u>			
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 <sup>2</sup> )	_____	_____	_____
Area x Attenuation factor (mm <sup>2</sup> )	_____	_____	_____
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<sup>2</sup>) \_\_\_\_\_  
Peak area x attenuation (mm<sup>2</sup>) \_\_\_\_\_  
Calculated concentration (ppm) \_\_\_\_\_  
Deviation (%) \_\_\_\_\_

### 4. Audit samples

	<u>Sample 1</u>	<u>Sample 2</u>
Retention time (min)	_____	_____
Injection time 24-hour basis)	_____	_____
Attenuation factor	_____	_____
Peak height (mm)	_____	_____
Peak area (mm <sup>2</sup> )	_____	_____
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.

## APPARATUS FOR PREPARING STANDARD GAS MIXTURES

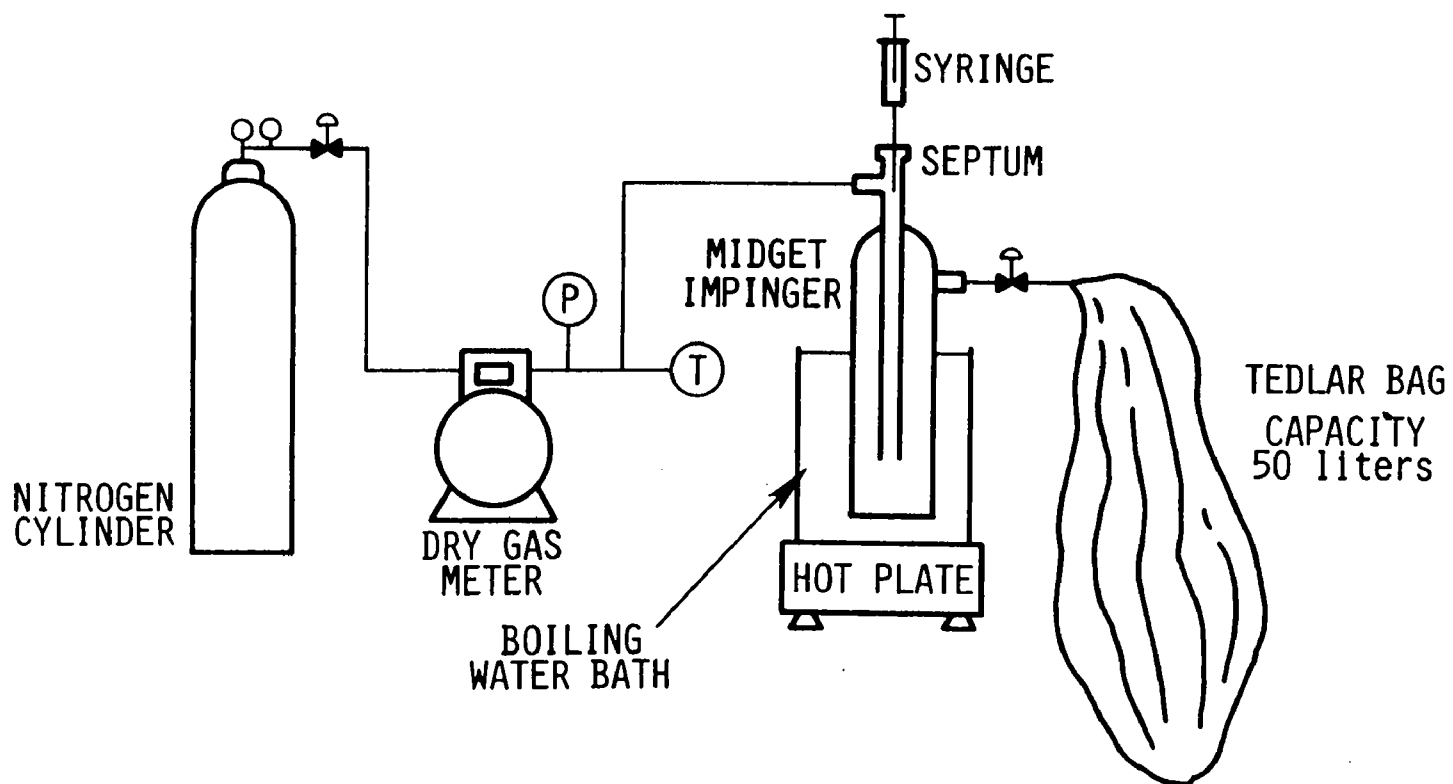


FIGURE 18-8.

# INTEGRATED BAG SAMPLING TRAIN

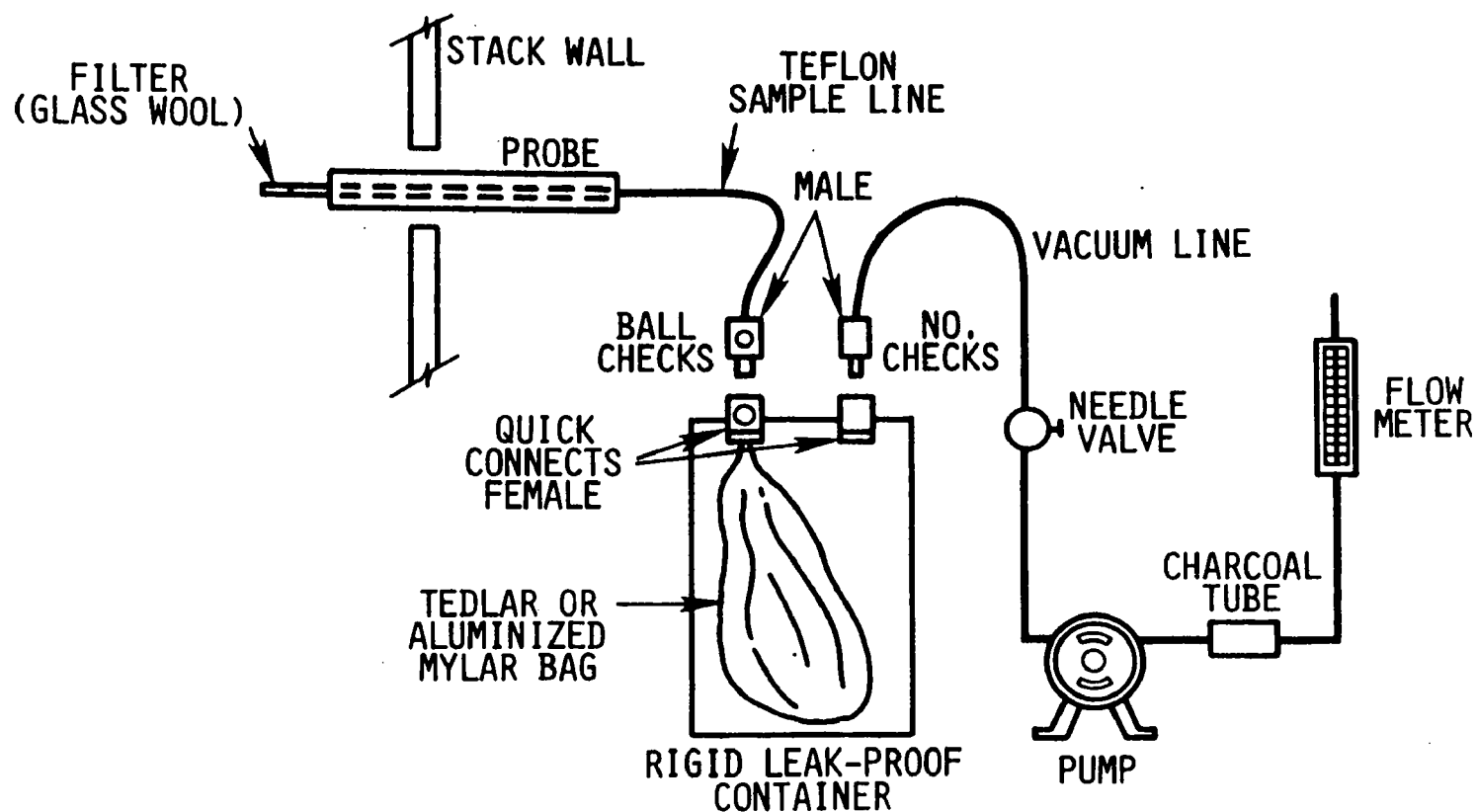


FIGURE 18-9.

# EXPLOSION RISK GAS SAMPLING METHOD

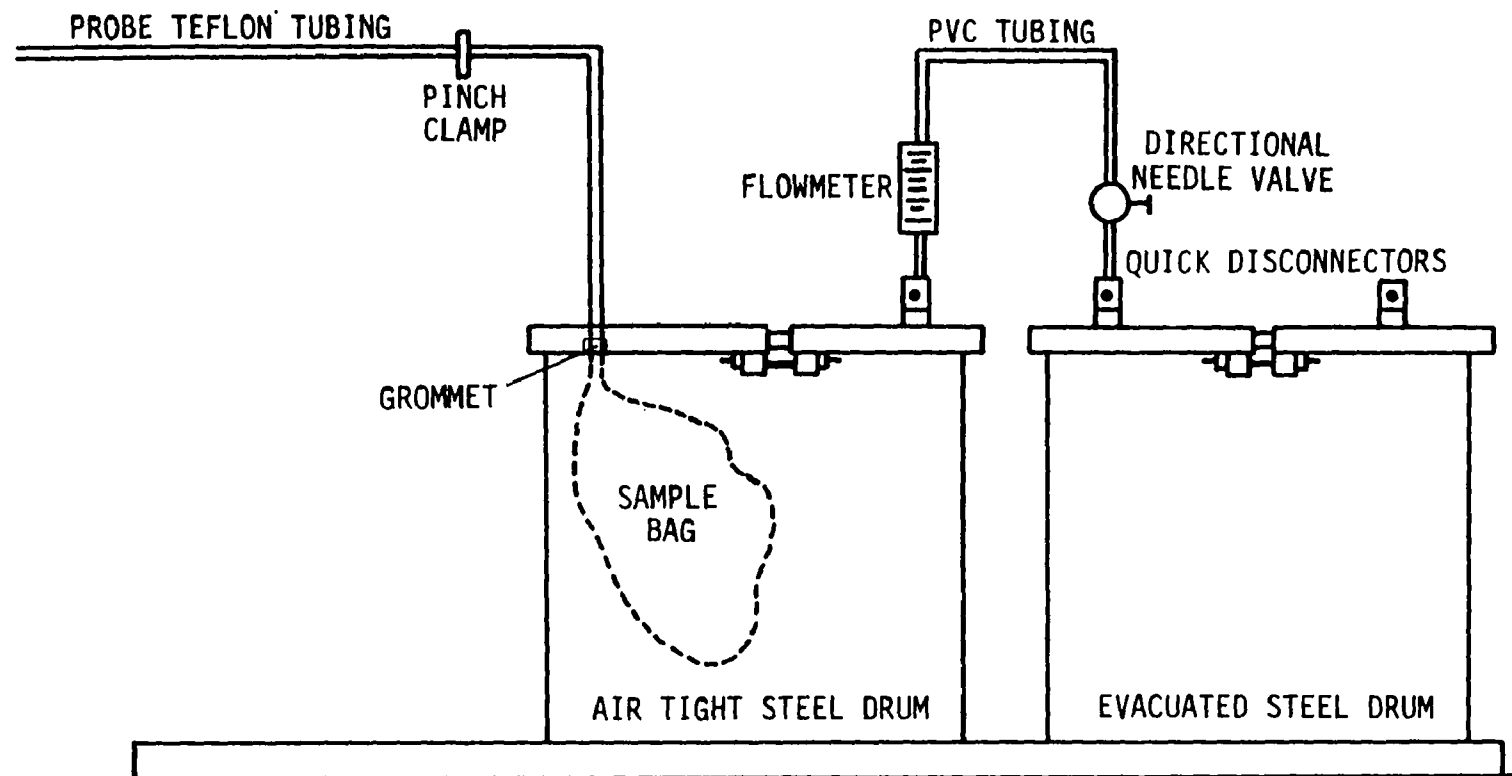


FIGURE 19-9a.

Plant \_\_\_\_\_ Date \_\_\_\_\_

Site \_\_\_\_\_

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>
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 _____			
<u>Components</u>	<u>Area</u>	<u>Attenuation</u>	<u>A x A Factor</u>	<u>Conc. (ppm)</u>
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

Run No. _____	Time _____			
<u>Components</u>	<u>Area</u>	<u>Attenuation</u>	<u>A x A Factor</u>	<u>Conc. (ppm)</u>
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

Run No. _____	Time _____			
<u>Components</u>	<u>Area</u>	<u>Attenuation</u>	<u>A x A Factor</u>	<u>Conc. (ppm)</u>
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

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

# DIRECT INTERFACE SAMPLING SYSTEM

18-51

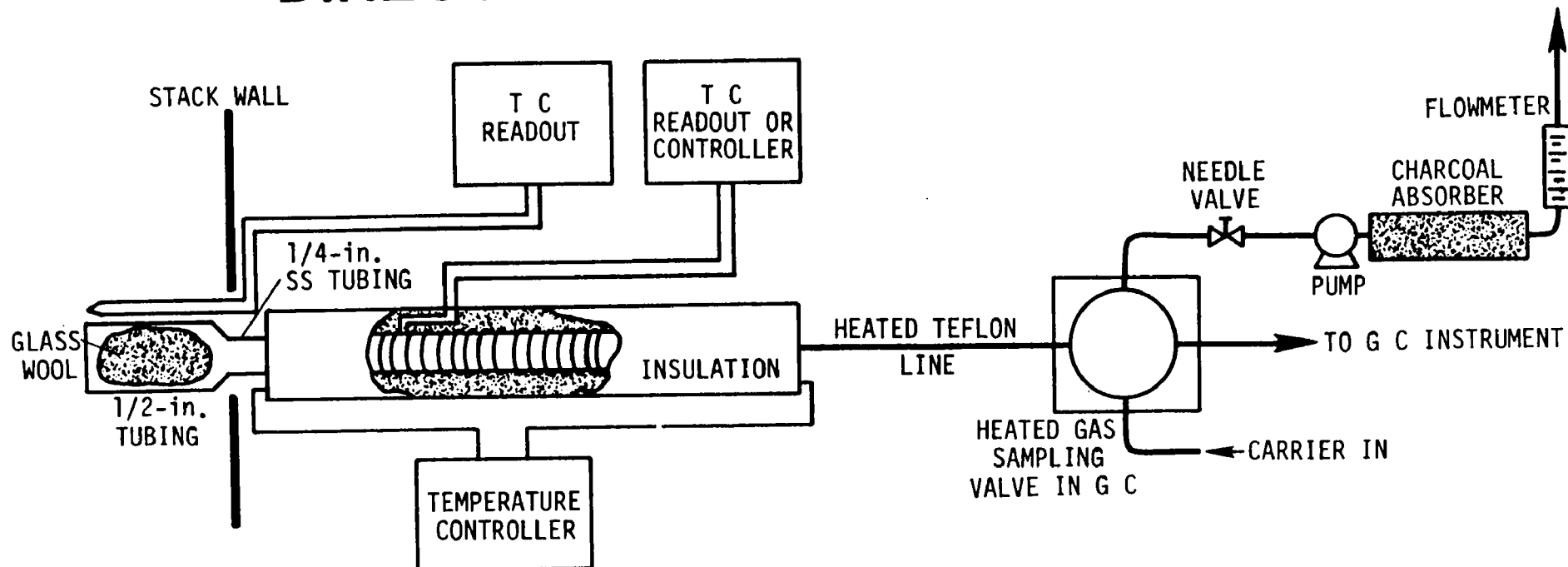


FIGURE 18-12.

# DIAGRAM OF THE HEATED BOX REQUIRED FOR DILUTION OF SAMPLE GAS

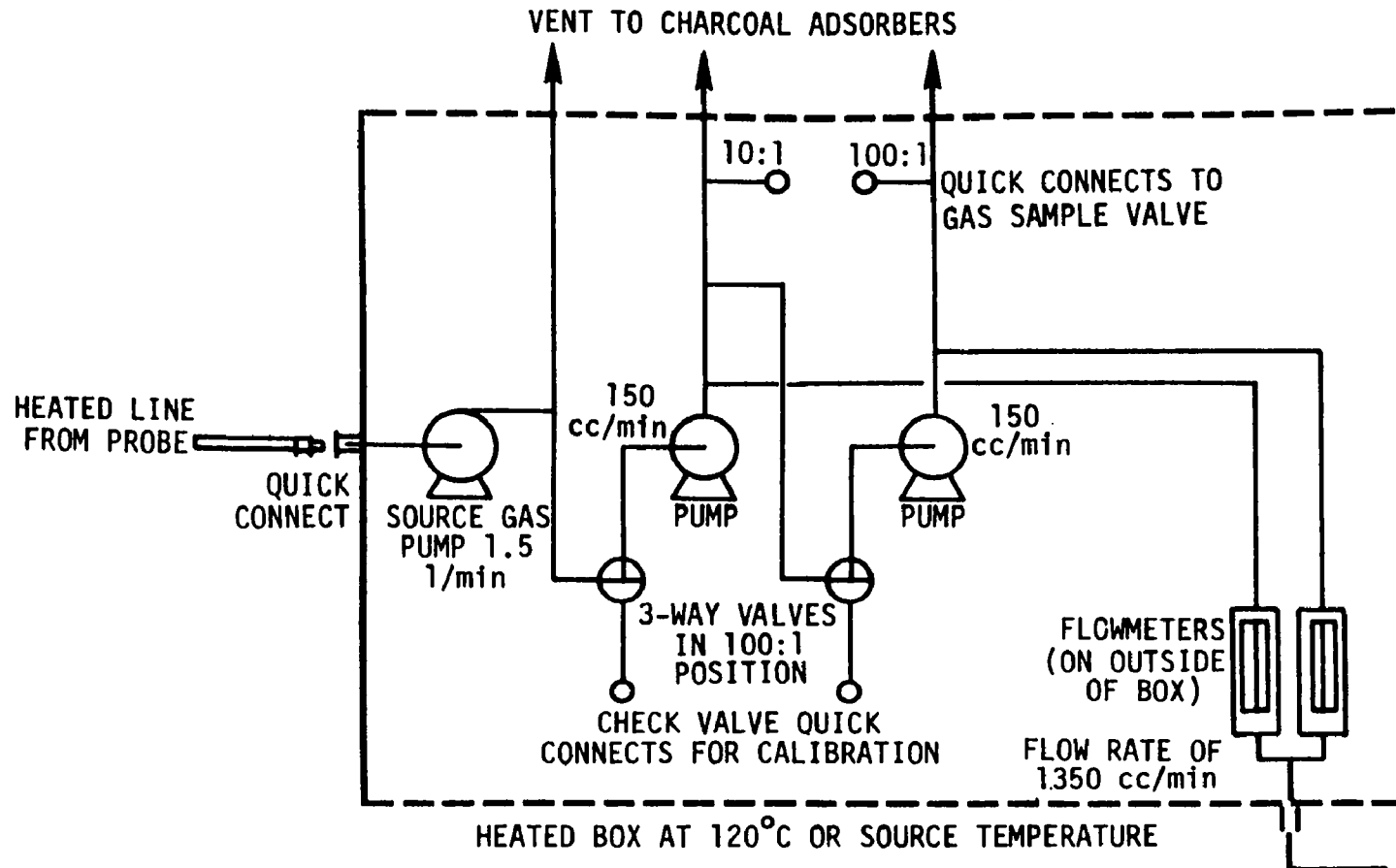


FIGURE 18-13.

**Gaseous Organic Sampling and Analysis Check List**  
**(Respond with initials or number as appropriate)**

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

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.

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 programmable 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  $\pm 2$  percent, for preparation 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. 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.

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 compatibility 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 parts 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 50° 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. Follow 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 determine 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:

$$Q_2 = Q_1 \left( \frac{P_1 T_2}{P_2 T_1} \right)^{1/2} \text{ Eq. 18-1}$$

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:

$$C_a = \frac{10^6 \bar{X}_a q_a}{q_a + q_d} \text{ Eq. 18-2}$$

Where:

$C_a$  = Concentration of component "a" in ppm.  
 $\bar{X}_a$  = 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:

$$C_a = 10^6 \bar{X}_a \left( \frac{q_{a1}}{q_{d1} + q_{a1}} \right) \left( \frac{q_{a2}}{q_{d2} + q_{a2}} \right) \text{ Eq. 18-3}$$

Where:

$C_a$  = Concentration of component "a" in ppm.

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

$q_{a1}$  = Flow rate of component "a" in stage 1.

$q_{d1}$  = Flow rate of component "a" in stage 2.

$q_{a2}$  = 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-capped 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:

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

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Where:

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

$L$  = 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 attenuator 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, attenuator 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.

**8.4 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 30178, 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 16-3 and 16-7. 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<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O), 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 16-9. 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 16-10. 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 16-9a). 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 midjet 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 6 to 5°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 organic(s) 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  $\pm 1$  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 1000/200 mg for silica gel tubes. As an alternative, the tubes may contain a porous polymer adsorbent such as Tenax GC or KAD-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 manufacturer'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 80 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 within 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 6550-60-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<sub>2</sub>O, Data source \_\_\_\_\_  
 Moisture content \_\_\_\_\_ %, Data source \_\_\_\_\_  
 Particulate content \_\_\_\_\_, Data source \_\_\_\_\_

Baseous components

N <sub>2</sub> _____ %	Hydrocarbons _____ ppm
O <sub>2</sub> _____ %	_____
CO _____ %	_____
CO <sub>2</sub> _____ %	_____
SO <sub>2</sub> _____ %	_____

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:

<u>Compound</u>	<u>Retention time</u>	<u>Attenuation</u>
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

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 (mm²)				
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 <sup>a</sup>	Flow rate (lab conditions) <sup>b</sup>

- <sup>a</sup> Vol. of gas may be measured in milliliters, liters or cubic feet.  
<sup>b</sup> 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.



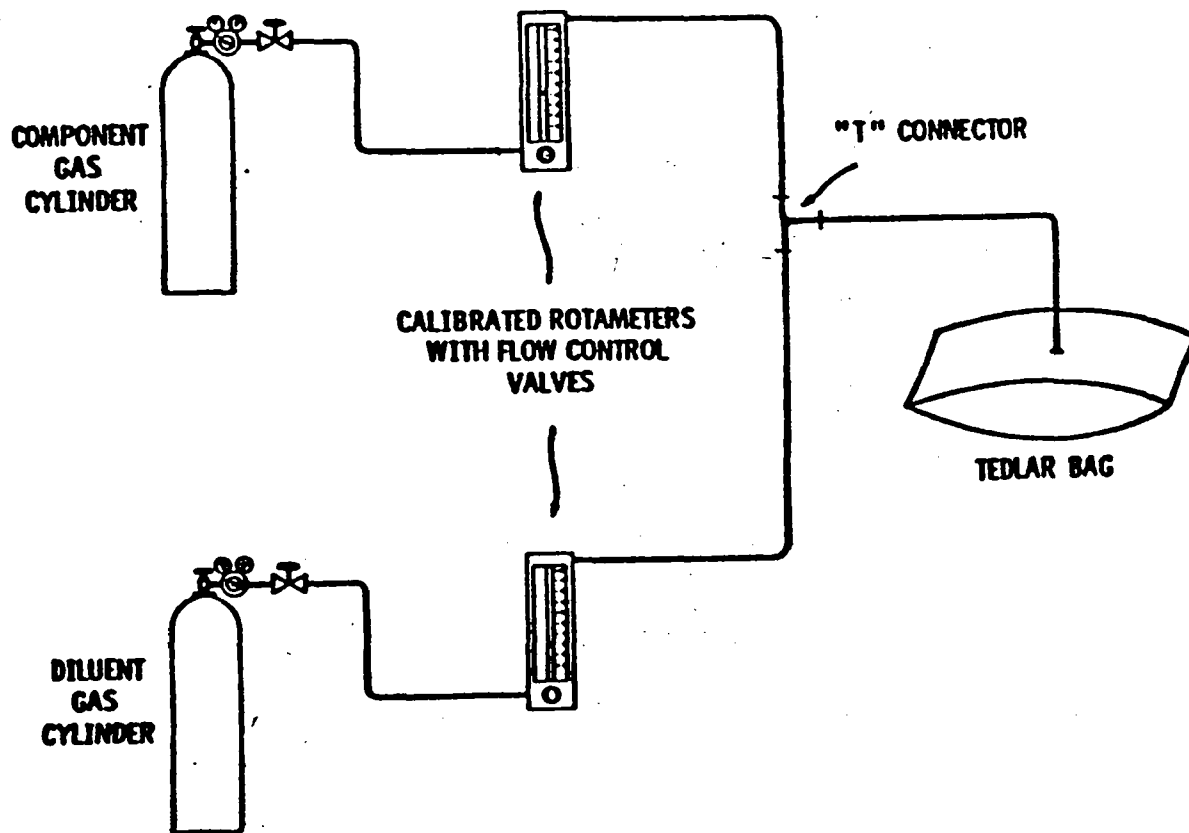


Figure 18-5. Single-stage calibration gas dilution system.

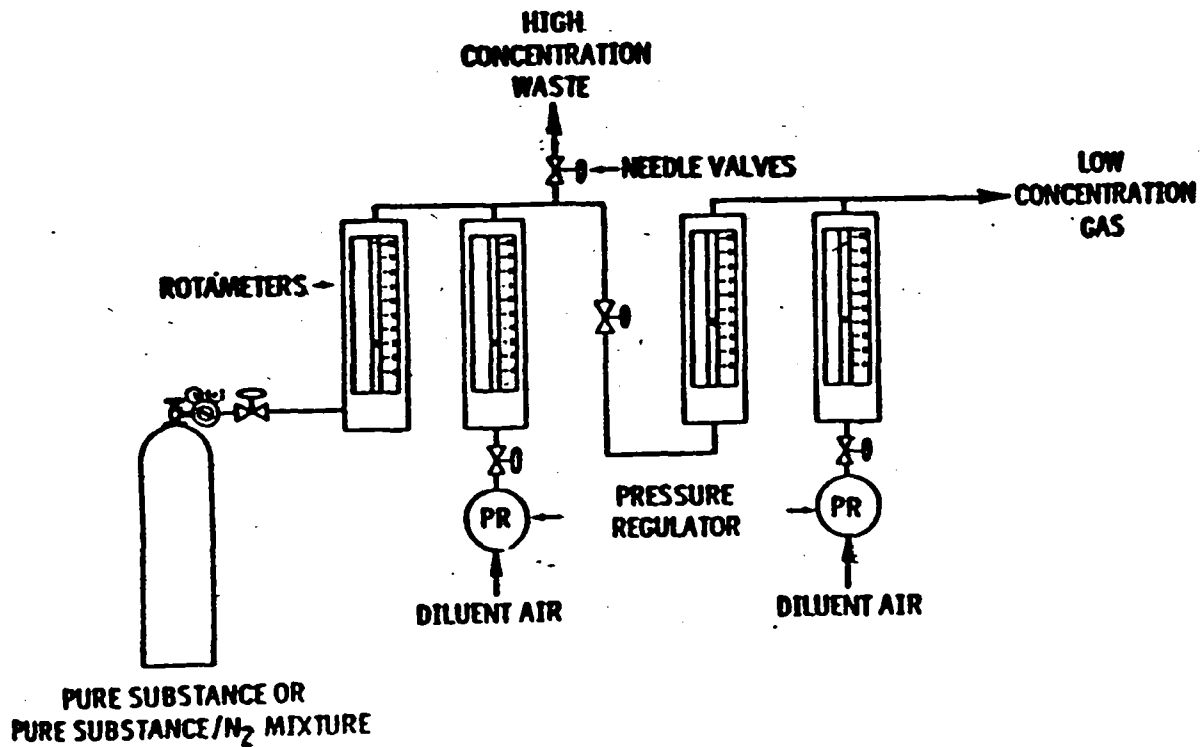


Figure 18-6. Two-stage dilution apparatus.

## 1. High concentration as mixture

Component \_\_\_\_\_ Concentration \_\_\_\_\_ ppm

Diluent gas \_\_\_\_\_

## 2. Dilution and analysis etc

Date \_\_\_\_\_

Stage 1Mixture 1 Mixture 2 Mixture 3

Component gas-rotameter reading \_\_\_\_\_

Diluent gas-rotameter reading \_\_\_\_\_

Ambient temp. (°C) \_\_\_\_\_

Manometer reading, inches H<sub>2</sub>O \_\_\_\_\_

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<sup>2</sup>) \_\_\_\_\_Area x Attenuation factor (mm<sup>2</sup>) \_\_\_\_\_

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<sup>2</sup>) \_\_\_\_\_Peak area x attenuation (mm<sup>2</sup>) \_\_\_\_\_

Calculated concentration (ppm) \_\_\_\_\_

Deviation (%) \_\_\_\_\_

## 4. Audit samples

Sample 1Sample 2

Retention time (min) \_\_\_\_\_

Injection time 24-hour basis) \_\_\_\_\_

Attenuation factor \_\_\_\_\_

Peak height (mm) \_\_\_\_\_

Peak area (mm<sup>2</sup>) \_\_\_\_\_

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.

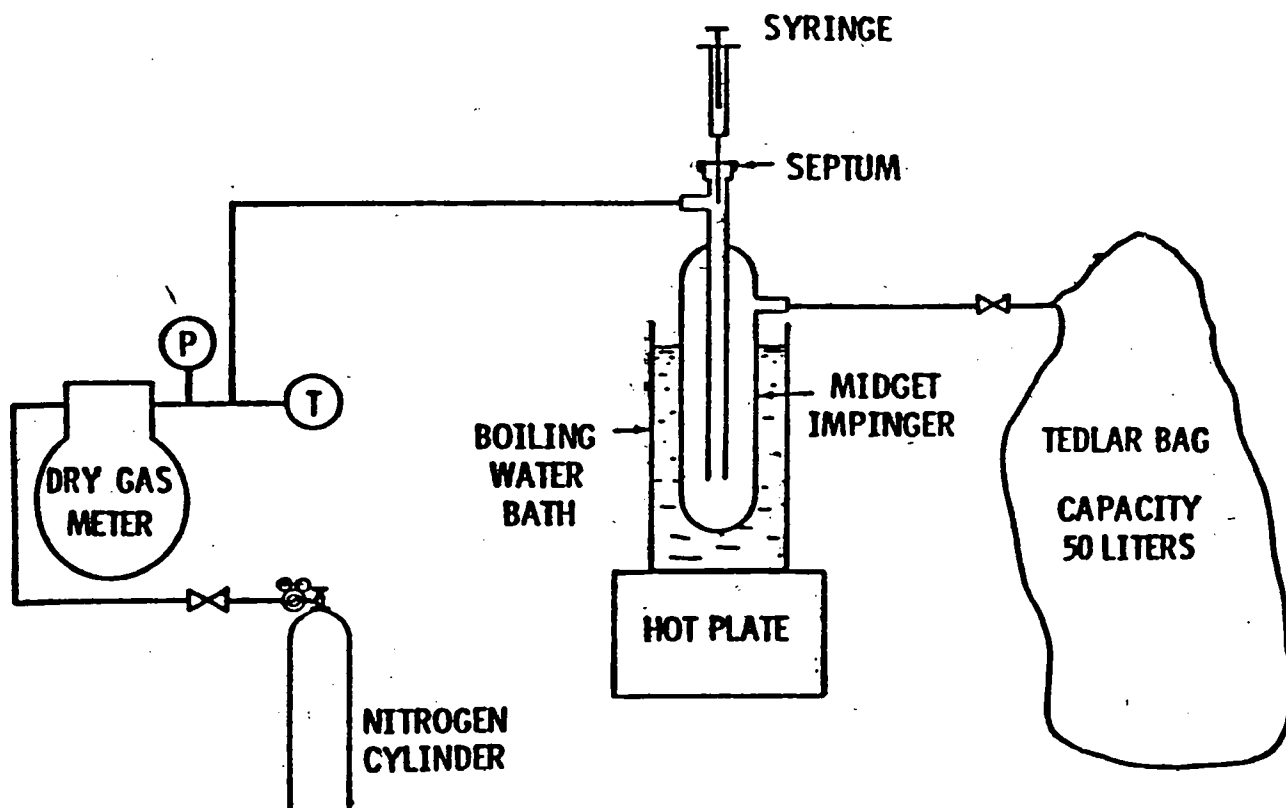


Figure 18-8. Apparatus for preparation of liquid materials.

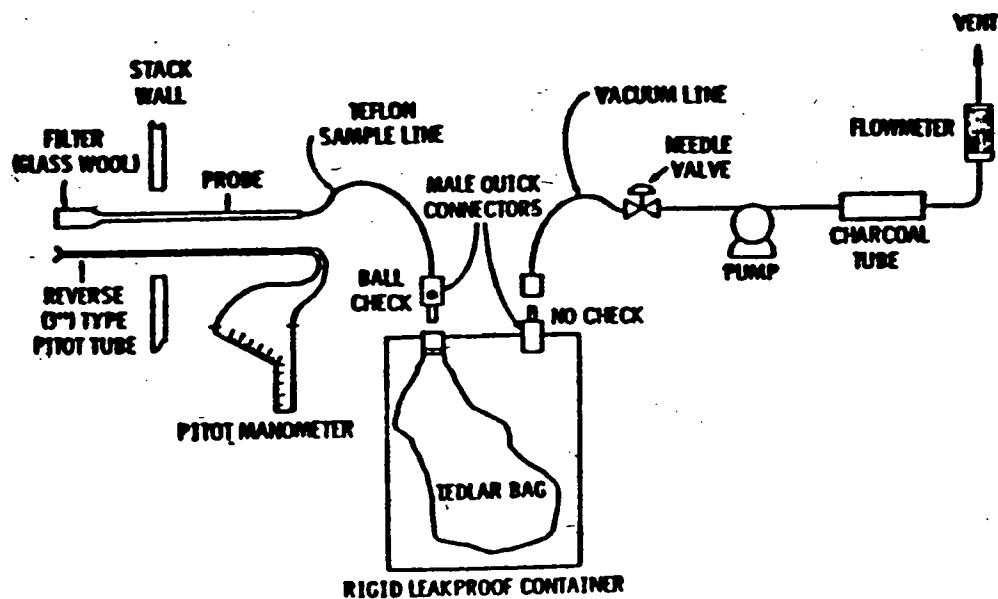


Figure 18-9. Integrated bag sampling train.

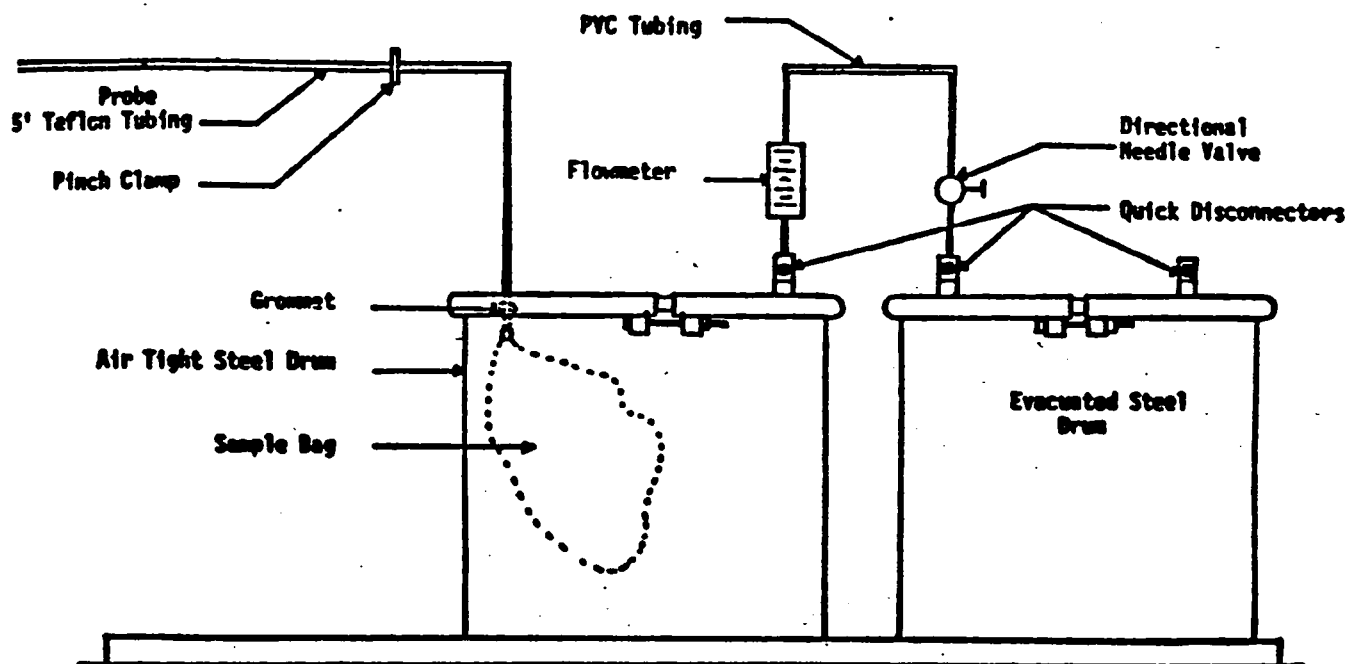


Figure 18-9a. Explosion risk gas sampling method.

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.

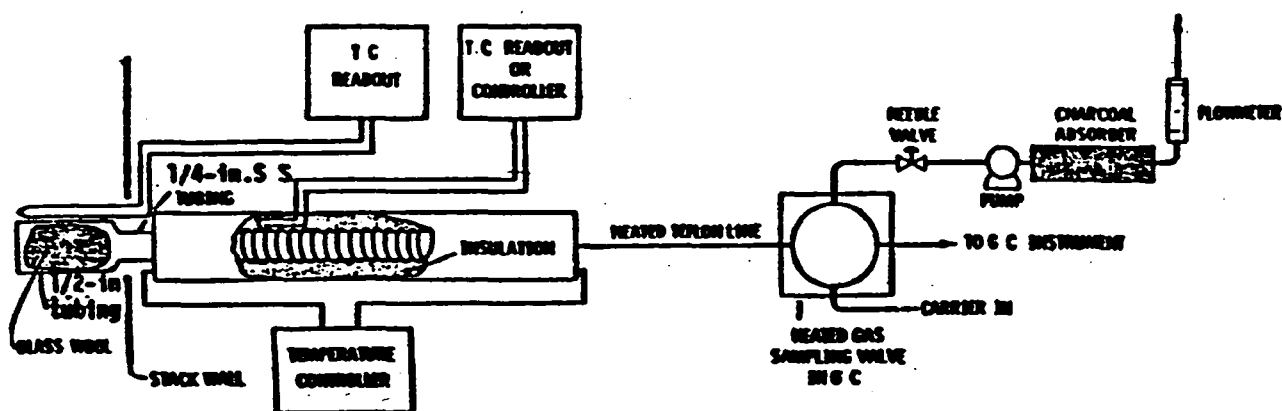


Figure 18-12. Direct interface sampling system.

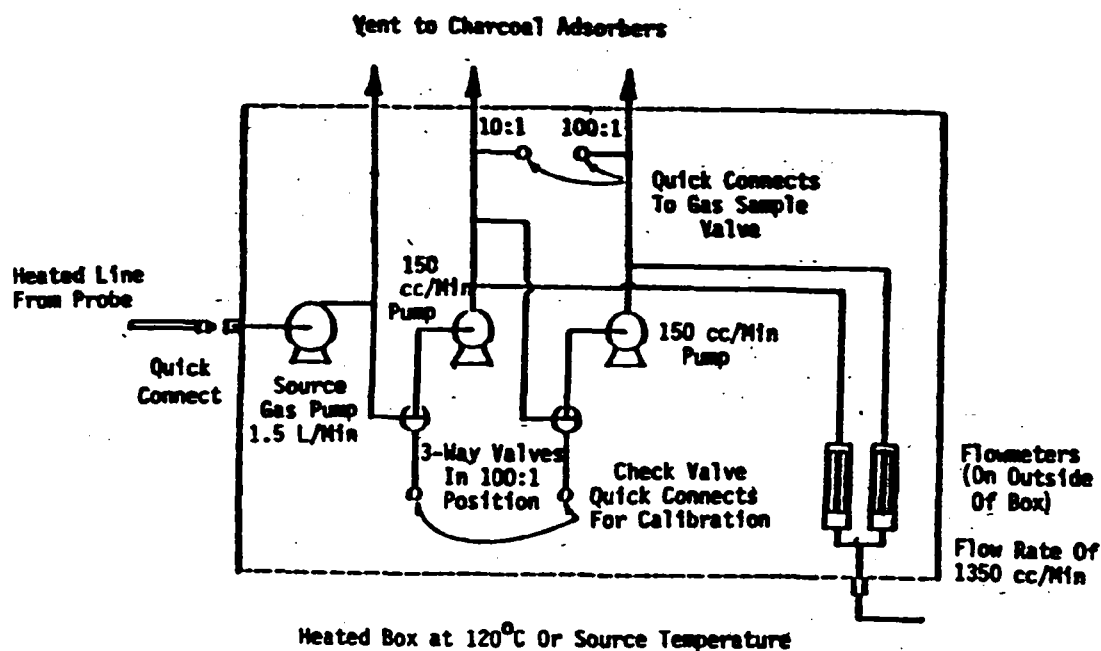


Figure 18-13. Schematic diagram of the heated box required for dilution of sample gas.

Gaseous Organic Sampling and Analysis  
Check List

(Respond with initials or number as appropriate)

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

	Source sample 1	Source sample 2	Source sample 3
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 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).....			

Figure 18-14. Sampling and analysis sheet.

METHOD 21. DETERMINATION OF VOLATILE  
ORGANIC COMPOUND LEAKS

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

2. Definitions

2.1 Leak Definition Concentration. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak)



is present. The leak definition is an instrument meter reading based on a reference compound.

2.2 Reference Compound. The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

2.3 Calibration Gas. The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

2.4 No Detectable Emission. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is not present. Since background VOC concentrations may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than a concentration corresponding to the minimum readability specification indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

2.5 Response Factor. The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

2.6 Calibration Precision. The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

2.7 Response Time. The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

### 3. Apparatus

#### 3.1 Monitoring Instrument.

##### 3.1.1 Specifications.

a. The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

b. The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

c. The scale of the instrument meter shall be readable to  $\pm 5$  percent of the specified leak definition concentration.

d. The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be 1/2 to 3 liters per minute.

e. The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association).

#### 3.1.2 Performance Criteria.

a. The instrument response factors for the individual compounds to be measured must be less than 10.

b. The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

c. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

d. The evaluation procedure for each parameter is given in Section 4.4.

#### 3.1.3 Performance Evaluation Requirements.

a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

3.2 Calibration Gases. The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, less than 10 ppmv VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within  $\pm 2$  percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternatively, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within  $\pm 2$  percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results.

#### 4. Procedures

4.1 Pretest Preparations. Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

4.2 Calibration Procedures. Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the

appropriate warmup period and zero or internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value. (Note: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.)

#### 4.3 Individual Source Surveys.

4.3.1 Type I - Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

a. Valves--The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where leaks could occur.

b. Flanges and Other Connections--For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

c. Pumps and Compressors--Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

d. Pressure Relief Devices--The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

e. Process Drains--For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

f. Open-Ended Lines or Valves--Place the probe inlet at approximately the center of the opening to the atmosphere.

g. Seal System Degassing Vents and Accumulator Vents--Place the probe inlet at approximately the center of the opening to the atmosphere.

h. Access Door Seals--Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

#### 4.3.2 Type II - "No Detectable Emission".

Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration described in 4.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) Pump or Compressor Seals--If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices--If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources

exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in this paragraph shall be used to determine if detectable emissions exist.

4.3.3 Alternative Screening Procedure. A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument techniques of 4.3.1 or 4.3.2.

Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or a squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks, as applicable. If any bubbles are observed, the instrument techniques of 4.3.1 or 4.3.2 shall be used to



determine if a leak exists, or if the source has detectable emissions, as applicable.

4.4 Instrument Evaluation Procedures. At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 Response Factor. Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 80 percent of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 90 percent of the saturation concentration, or 70 percent of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 5.

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas.

Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

## 5. Bibliography

5.1 DuBose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-051. September 1981.

5.2 Brown, G.E., et al. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-022. May 1981.

5.1 DuBose, D.A., et al. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-110. September 1981.

**1.1 Applicability.** This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

**1.2 Principle.** A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

## 2. Definitions.

**2.1 Leak Definition Concentration.** The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

**2.2 Reference Compound.** The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

**2.3 Calibration Gas.** The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

**2.4 No Detectable Emission.** The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is not present. Since background VOC concentrations may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than a concentration corresponding to the minimum readability specification indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

**2.5 Response Factor.** The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

**2.6 Calibration Precision.** The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

**2.7 Response Time.** The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

## 3. Apparatus.

### 3.1 Monitoring Instrument.

#### 3.1.1 Specifications.

a. The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

b. The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

c. The scale of the instrument meter shall be readable to 5 percent of the specified leak definition concentration.

d. The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be 1/2 to 3 liters per minute.

e. The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association).

#### 3.1.2 Performance Criteria.

a. The instrument response factors for the individual compounds to be measured must be less than 10.

b. The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

c. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

d. The evaluation procedure for each parameter is given in Section 4.4.

#### 3.1.3 Performance Evaluation Requirements.

a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

**3.2 Calibration Gases.** The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, less than 10 ppmv VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration as mixture are used, they must be analyzed and certified by the manufacturer to be within  $\pm 2$  percent

## Method 21. Determination of Volatile Organic Compound Leaks

### 1. Applicability and Principle.

accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternately, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within  $\pm 2$  percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results.

#### 4. Procedures.

4.1 *Pretest Preparations.* Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

4.2 *Calibration Procedures.* Assemble and start up the VOC analyzer according to the manufacturer's instructions. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

*Note.*—If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

#### 4.3 Individual Source Surveys.

4.3.1 *Type I—Leak Definition Based on Concentration.* Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements.

Examples of the application of this general technique to specific equipment types are:

a. *Valves.*—The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exists the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where leak could occur.

b. *Flanges and Other Connections.*—For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

c. *Pumps and Compressors.*—Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the

shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

d. *Pressure Relief Devices.*—The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

e. *Process Drains.*—For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

f. *Open-Ended Lines or Valves.*—Place the probe inlet at approximately the center of the opening to the atmosphere.

g. *Seal System Degassing Vents and Accumulator Vents.*—Place the probe inlet at approximately the center of the opening to the atmosphere.

h. *Access Door Seals.*—Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

#### 4.3.2 Type II—"No Detectable Emission".

Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration described in 4.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) *Pump or Compressor Seals.*—If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) *Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices.*—If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in this

paragraph shall be used to determine if detectable emissions exist.

4.3.3 *Alternative Screening Procedure.* A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument techniques of 4.3.1 or 4.3.2.

Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or a squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of 4.3.1 or 4.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

4.4 *Instrument Evaluation Procedures.* At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 *Response Factor.* Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 80 percent of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 80 percent of the saturation concentration, or 70 percent of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 5.

4.4.2 *Calibration Precision.* Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

**4.4.3 Response Time.** Introduce zero gas to the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

**5. Bibliography.**

**5.1 DuBose, D.A., and G.E. Harris.** Response Factors of VOC Analyzers at a

Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-051. September 1981.

**5.2 Brown, G.E., et al.** Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-022. May 1981.

**5.3 DuBose, D.A., et al.** Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-110. September 1981.

[FR Doc. 83-22488 Filed 8-17-83; 9:45 am]

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METHOD 23. DETERMINATION OF HALOGENATED  
ORGANICS FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, and trichlorotrifluoroethane in stack gases from sources as specified in the regulations. The method does not measure halogenated organics contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

2. Range and Sensitivity

The range of this method is 0.1 to 200 ppm. The upper limit may be extended by extending the calibration range or by diluting the sample.

### 3. Interferences

The chromatograph column with the corresponding operating parameters herein described normally provides an adequate resolution of halogenated organics; however, resolution interferences may be encountered in some sources. Therefore, the chromatograph operator shall select the column best suited to his particular analysis problem, subject to the approval of the Administrator. Approval is automatic provided that confirming data are produced through an adequate supplemental analytical technique, e.g. analysis with a different column or GC/mass spectroscopy. This confirming data must be available for review by the Administrator.

### 4. Apparatus

4.1 Sampling (see Figure 23-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex\* glass, or Teflon\* tubing (as stack temperature permits), each equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Line. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

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\*Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

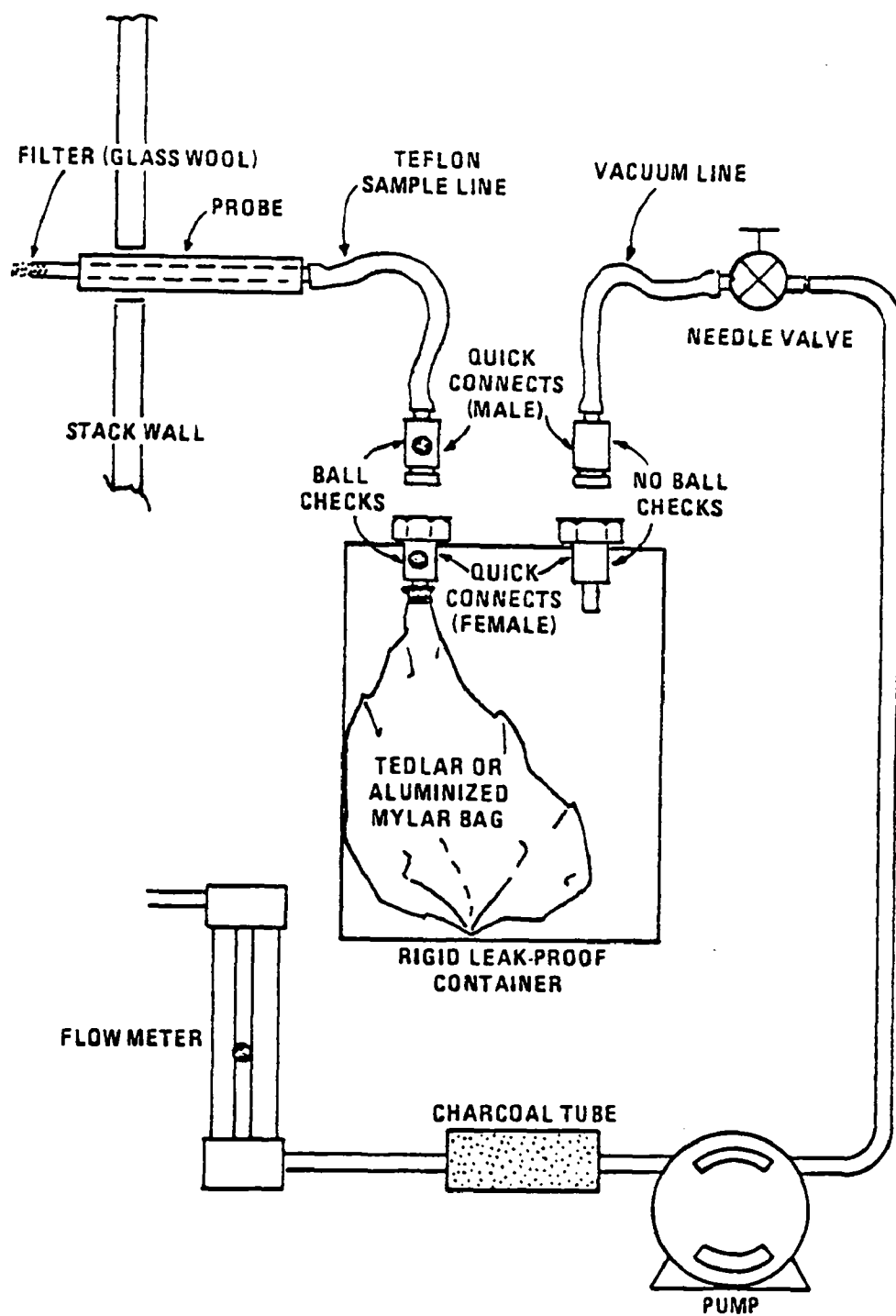


Figure 23-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)



4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 23-1.

4.1.4 Tedlar or Aluminized Mylar Bags. 100-liter capacity, to contain sample.

4.1.5 Bag Containers. Rigid leakproof containers for sample bags, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump. Leak-free, with minimum of 2-liters/min capacity.

4.1.8 Charcoal Tube. To prevent admission of halogenated organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

4.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 23-1).

4.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to gas chromatograph sample loop is required for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon conclusion of analysis of those bags.

4.3. Analysis. The following equipment is needed:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder, and 1.0- to 2.0-ml sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm of the halogenated organic compound that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Column. Stainless steel, 3.05 m by 3.2 mm, containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. The analyst may use other columns provided that the precision and accuracy of the analysis of standards are not impaired and he has available for review information confirming that there is adequate resolution of the halogenated organic compound peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the halogenated organic compound peak by an interferent peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromatographic Peak Resolution.")

4.3.3 Flow Meters (2). Rotameter type, 0-to-100-ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to 1°C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump. Leak-free, with a minimum of 100-ml/min capacity.

4.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator (4.3.8), to measure chromatograph peak areas.

4.4 Calibration. Sections 4.4.2 through 4.4.6 are for the optional procedure in Section 7.1.

4.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 25- $\mu$ l, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.4 Syringe. 50- $\mu$ l, gas tight, individually calibrated to dispense liquid halogenated organic solvent.

4.4.5 Dry Gas Meter, with Temperature and Pressure Gauges. Accurate to  $\pm 2$  percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize solvent.

## 5. Reagents

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis. The following are needed for analysis:

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air. Zero grade, as required by the detector.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Halogenated Organic Compound, 99 Mol Percent Pure. Certified by the manufacturer to contain a minimum of 99 Mol percent of the particular halogenated organic compound; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (200, 100, and 50 ppm of the halogenated organic compound of interest, in nitrogen). The tester may use these cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 5.2.3.1).

(b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified concentration of the halogenated organic compound, and recommended maximum shelf life to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the halogenated organic compound in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration

calibration standard (between 200 and 400 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 100 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 Mol percent of the halogenated organic compounds) in accordance with the procedure described in Section 7.1 or by (b) having it analyzed by the National Bureau of Standards, if such analysis is available. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person

supervising the analysis samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (the halogenated organic compounds of interest, in nitrogen). The concentrations of the audit cylinders should be: one low-concentration cylinder in the range of 25 to 50 ppm, and one high-concentration cylinder in the range of 200 to 300 ppm. When available, the tester may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at the Environmental Protection Agency, the tester must secure an alternative source.

## **6. Procedure**

**6.1 Sampling.** Assemble the sampling train as shown in Figure 23-1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. 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 that will more than half fill the bag in the specified sample period. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel.

Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. 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. Protect bag container from sunlight.

6.2 Sample Storage. Keep the sample bags out of direct sunlight and protect from heat. Perform the analysis within 1 day of sample collection for methylene chloride, ethylene dichloride, and trichlorotrifluoroethane, and within 2 days for perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and carbon tetrachloride.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 0-to-100-ml/min rotameter with flow control valve followed by a charcoal tube and a 0-to-1-in.  $H_2O$  pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.



6.4 Analysis. Set the column temperature to 100°C and the detector temperature to 225°C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. Purge the sample loop for 30 sec at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed, and the attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to the halogenated organic compound, as determined in Section 7.2.1. Measure the halogenated organic compound peak area,  $A_m$ , by use of a disc integrator, electronic integrator, or a planimeter. Record  $A_m$  and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

#### 6.5 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.)

### 7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance

7.1 Preparation of Standard Gas Mixtures. (Optional procedure--delete if cylinder standards are used.) Assemble the apparatus shown in Figure 23-2. Check that all fittings are tight. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. Refer to Table 23-1. While the bag is filling, use the 50- $\mu$ l syringe to inject through the septum on top of the impinger, the quantity required to yield a concentration of 200 ppm. In a like manner, use the 25- $\mu$ l syringe to prepare bags having approximately 100- and 50-ppm concentrations. To calculate the specific concentrations, refer to Section 8.1. (Tedlar bag gas mixture standards of methylene chloride, ethylene dichloride, and trichlorotrifluoroethane may be used for

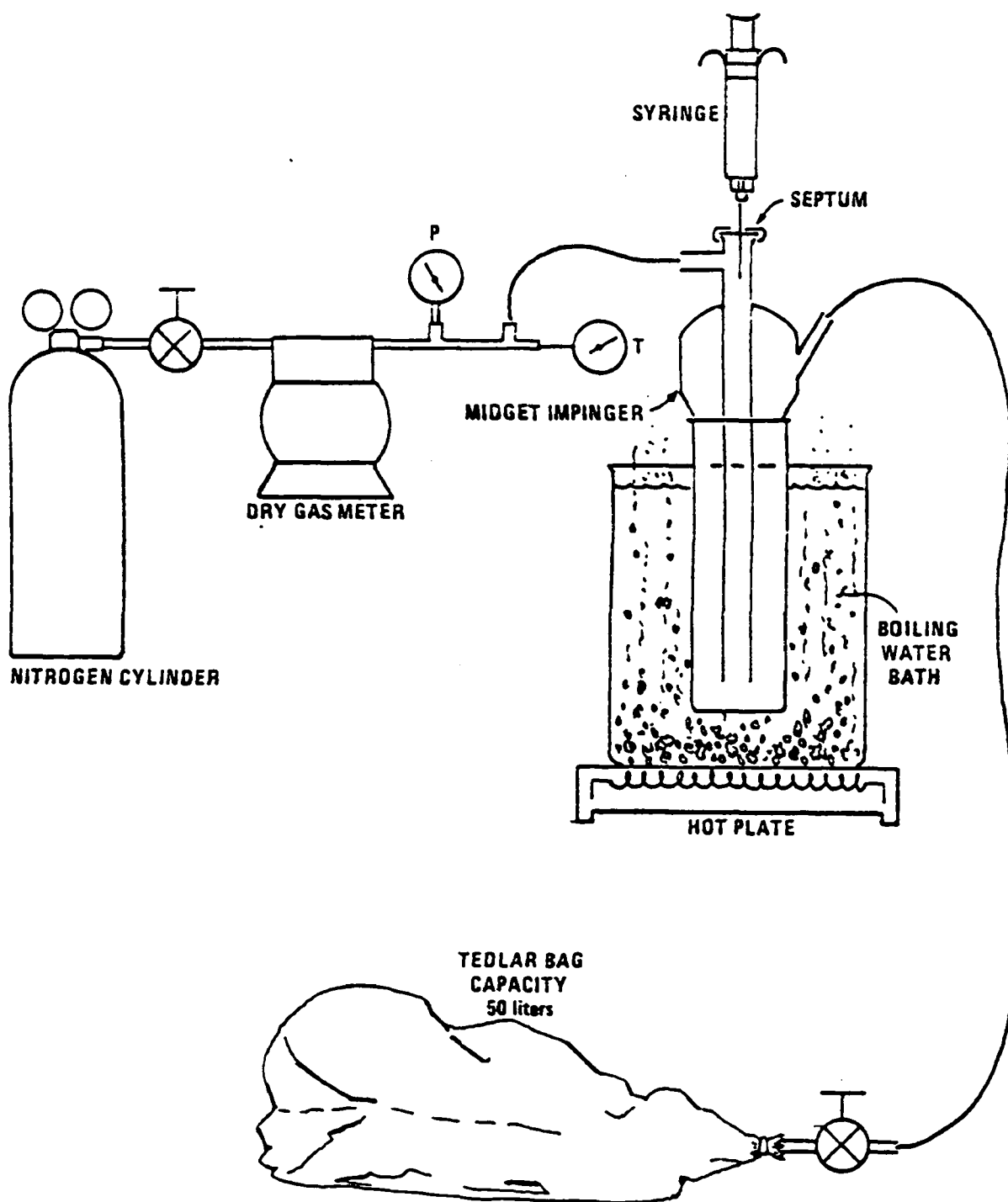


Figure 23-2. Preparation of standards (optional).

TABLE 23-1. INJECTION VALUES FOR PREPARATION OF STANDARDS (Optional, See Section 7.1)

Compound	Molecular Weight g/g-mole	Density at 293°K g/ml	μl/50 liters of N <sub>2</sub> required for approximate concentration of:		
			200 ppm	100 ppm	50 ppm
Perchloroethylene C <sub>2</sub> Cl <sub>4</sub>	165.85	1.6230	42.5	21.2	10.6
Trichloroethylene C <sub>2</sub> HCl <sub>3</sub>	131.40	1.4649	37.3	18.6	9.3
1,1,1-Trichloroethane C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	133.42	1.4384	38.6	19.3	9.6
Methylene Chloride CH <sub>2</sub> Cl <sub>2</sub>	84.94	1.3255	26.6	13.3	6.7
Trichlorotrifluoroethane C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>	187.38	1.5790	49.3	24.7	12.3
Carbon Tetrachloride CCl <sub>4</sub>	153.84	1.5940	40.1	20.1	10.0
Ethylene Dichloride C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	98.96	1.2569	32.7	16.4	8.2

1 day, trichloroethylene and 1,1,1-trichloroethane for 2 days, and perchloroethylene and carbon tetrachloride for 10 days from the date of preparation. (Caution: If the new gas mixture standard is a lower concentration than the previous gas mixture standard, contamination may be a problem when a bag is reused.)

## 7.2 Calibration.

7.2.1 Determination of Halogenated Organic Compound Retention Time. (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed, and the attenuator setting. Record peaks and detector responses that occur in the absence of the halogenated organic. Maintain conditions (with the equipment plumbing arranged identically to Section 6.3), flush the sample loop for 30 sec at the rate of 100 ml/min with one of the halogenated organic compound calibration mixtures, and activate the sample valve. Record the injection time. Select the peak that corresponds to the halogenated organic compound. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart

speed is defined as the halogenated organic compound peak retention time. Since it is possible that there will be other organics present in the sample, it is very important that positive identification of the halogenated organic compound peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 sec at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record  $C_c$ , the concentration of halogenated organic injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

### 7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix E, Supplement B: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks by connecting a water manometer and pressurizing the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O) and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

## 8. Calculations.

### 8.1 Optional Procedure Standards Concentrations.

Calculate each halogenated organic standard concentration ( $C_c$  in ppm) prepared in accordance with Section 7.1 as follows:

$$C_c = \frac{\frac{BD}{M} (24.055 \times 10^3)}{V_m Y \frac{293}{T_m} \frac{P_m}{760}} = 6.240 \times 10^4 \frac{BD T_m}{M V_m Y P_m}$$

Eq. 23-1

Where:

- B = Volume of halogenated organic injected,  $\mu\text{l}$ .
- D = Density of compound at 293°K, g/ml.
- M = Molecular weight of compound, g/g-mole.
- $V_m$  = Gas volume measured by dry gas meter, liters.
- Y = Dry gas meter calibration factor, dimensionless.
- $P_m$  = Absolute pressure of dry gas meter, mm Hg.
- $T_m$  = Absolute temperature of dry gas meter, °K.
- 24.055 = Ideal gas molal volume at 293° K and 760 mm Hg, liters/g-mole.
- $10^3$  = Conversion factor. [(ppm)(ml)]/ $\mu\text{l}$ .

8.2 Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of  $C_c$  that corresponds to  $A_c$ . Calculate  $C_s$ , the concentration of halogenated organic in the sample (in ppm), as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1 - S_{wb})} \quad \text{Eq. 23-2}$$



Where:

- $C_c$  = Concentration of the halogenated organic indicated by the gas chromatograph, ppm.
- $P_r$  = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.
- $T_i$  = Sample loop temperature at the time of analysis, °K.
- $P_i$  = Laboratory pressure at time of analysis, mm Hg.
- $T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K.
- $S_{wb}$  = Water vapor content of the bag sample, volume fraction.

## 9. References

1. Fearheller, W.R., A.M. Kemmer, B.J. Warner, and D.Q. Douglas. Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. EPA Contract No. 68-02-1404, Task 33 and 68-02-2818, Work Assignment 3. January 1978. Revised by EPA August 1978.
2. Supelco, Inc. Separation of Hydrocarbons. Bulletin 747. Bellefonte, Pennsylvania. 1974.
3. Communication from Joseph E. Knoll. Perchloroethylene Analysis by Gas Chromatography. March 8, 1978.
4. Communication from Joseph E. Knoll. Test Method for Halogenated Hydrocarbons. December 20, 1978.

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 D 1475-60 (Reapproved 1980). Standard Test Method for Density of Paint, Lacquer, and Related Products (incorporated by reference - see §60.17).

2.2 ASTM D 2369-81. Standard Test Method for Volatile Content of Paints (incorporated by reference - see §60.17).

2.3 ASTM D 3792-79. Standard Test Method for Water Content in Water Reducible Paint by Direct Injection into a Gas Chromatograph (incorporated by reference - see §60.17).

2.4 ASTM D 4017-81. Standard Test Method for Water in Paints or 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 D 2369-81 (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:

$$W_V = \frac{W_1 - W_2}{W_3} \quad \text{Eq. 24-1}$$

Record the arithmetic average ( $\bar{W}_V$ ).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water ( $W_W$ ) using either "Standard Test Method for Water Content in Water Reducible Paint by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint or Related Coatings by the Karl Fischer Titration 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 ( $\bar{W}_W$ ).

3.3 Coating Density. Determine the density ( $D_c$ , kg/liter) of the surface coating using the procedure in ASTM D 1475-60 (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 ( $\bar{D}_c$ ).

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% $\bar{W}_v$	4.7% $\bar{W}_v$
Water Content, $W_w$	2.9% $\bar{W}_w$	7.5% $\bar{W}_w$
Density, $D_c$	0.001 kg/liter	0.002 kg/liter

4.3 Sample Analysis Criteria. For  $W_v$  and  $W_w$ , run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For  $D_c$  run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the 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.

$$W_0 = W_V \quad \text{Eq. 24-2}$$

Where:

$W_0$  = Weight fraction nonaqueous volatile matter, g/g.

#### 5.1.2 Waterborne Coatings.

$$W_0 = W_V - W_W \quad \text{Eq. 24-3}$$

### 5.2 Weight fraction solids.

$$W_S = 1 - W_V \quad \text{Eq. 24-4}$$

Where:  $W_S$  = Weight solids, g/g.

## 6. Bibliography

### 6.1 Provisional Method Test for Volatile Content of Paints.

Available from: Chairman, Committee D-1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 2359-81.

6.2 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. In: 1974 Book of ASTM Standards, Part 27. Philadelphia, Pennsylvania, ASTM Designation D 1475-60. 1980.

6.3 Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph. Available from: Chairman, Committee D-1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 3792-79.

6.4 Provisional Method of Test Water in Paint or Related Coatings by the Karl Fischer Titration Method. Available from: Chairman, Committee D-1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

# 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 D 1475-80. Standard Method of Test for Density of Paint, Lacquer, and Related Products.

2.2 ASTM D 2369-81. Provisional Method of Test for Volatile Content of Paints.

2.3 ASTM D 3792-79. Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph.

2.4 ASTM Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method.

## 3. Procedure

3.1 Volatile Matter Content. Use the procedure in ASTM D 2369-81 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:

$$W_v = \frac{W_1 - W_2}{W_3} \quad \text{Eq. 24-1}$$

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 Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph" or "Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method." 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 D 1475-80.

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average ( $D_c$ ).

3.4 Solids Content. Determine the volume fraction ( $V_s$ ) solids of the coating by calculation using the manufacturer's formulation.

## 4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, $W_v$ , . . . . .	1.5 pct $W_v$ . . . . .	4.7 pct $W_v$ . . . . .
Water content, $W_w$ , . . . . .	2.9 pct $W_w$ . . . . .	7.5 pct $W_w$ . . . . .
Density, $D_c$ , . . . . .	0.001 kg/liter . . . . .	0.002 kg/liter . . . . .

4.3 Sample Analysis Criteria. For  $W_v$  and  $W_w$ , run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For  $D_c$ , run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency.

Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the 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.

$$W_v = W_v \quad \text{Eq. 24-2}$$

Where:

$W_v$  = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_v = W_v - W_w \quad \text{Eq. 24-3}$$

5.2 Weight fraction solids.

$$W_s = 1 - W_v \quad \text{Eq. 24-4}$$

Where:  $W_s$  = Weight solids, g/g.

## 6. Bibliography

6.1 Provisional Method Test for Volatile Content of Paints. Available from: Chairman, Committee D-1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 2369-81.

6.2 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. In: 1980 Book of ASTM Standards, Part 27. Philadelphia, Pennsylvania, ASTM Designation D 1475-80, 1980.

6.3 Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph. Available from: Chairman, Committee D-1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 3792-79.

6.4 Provisional Method of Test Water in Paint or Related Coatings by the Karl Fischer Titration Method. Available from: Chairman, Committee D-1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.



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  $120 \pm 2^{\circ}\text{C}$  and an absolute pressure of  $510 \pm 51$  mm Hg for 4 hours. Alternatively,

a forced draft oven capable of maintaining a temperature of  $120 \pm 2^\circ\text{C}$  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  $510 \pm 51$  mm Hg and a temperature of  $120 \pm 2^\circ\text{C}$  for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of  $120 \pm 2^\circ\text{C}$  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, which is incorporated by reference. Make a total of three determinations for each coating. Report the density  $\overline{D_c}$  as the arithmetic average of the three determinations. This Standard Test Method For Density of Paint, Varnish, Lacquer, and Related Products can be found in the "1974 Annual Book of ASTM Standards." It is available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. It is also available for inspection at the Office of the Federal

Register Information Center, Room 8301, 1100 L Street, N.W., Washington, D.C. 20408. This incorporation by reference was approved by the Director of the Federal Register on \_\_\_\_\_, 1981. This material is incorporated as it exists on the date of the 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. Make a total of three determinations for each coating. Report the density  $\overline{D}_0$  as the arithmetic average of the three determinations.

### 3. Calculations

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content  $W_0$  using the following equation:

$$W_0 = \frac{M_{x1} + M_{cY1} - M_{cY2} - M_{x2}}{M_{cY1} - M_{cY2}} \quad \text{Eq. 24A-1}$$

Report the weight fraction VOC  $\overline{W}_0$  as the arithmetic average of the three determinations.

3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content  $V_0$  using the following equation:

$$V_0 = \frac{\overline{W}_0 \overline{D}_c}{\overline{D}_0} \quad \text{Eq. 24A-2}$$

4. Bibliography

4.1 Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. In: 1974 Book of ASTM Standards, Part 25, Philadelphia, Pennsylvania, ASTM Designation D 1475-60. 1974. p. 231-233.

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.

## Appendix A—Reference 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  $120 \pm 2^\circ\text{C}$  and an absolute pressure of  $510 \pm 51$  mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of  $120 \pm 2^\circ\text{C}$  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 ( $M_{s1}$ ).

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 ( $M_{cyl1}$ ). 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 ( $M_{cyl2}$ ). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of  $510 \pm 51$  mm Hg and a temperature of  $120 \pm 2^\circ\text{C}$  for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of  $120 \pm 2^\circ\text{C}$  for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight ( $M_d$ ). Repeat this procedure for a total of three determinations for each sample.

2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D 1475-60 (Reapproved 1980), which is incorporated by reference. It is available from the American Society of Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. It is also available for inspection at the Office of the Federal Register, Room 8401, 1100 L Street, NW., Washington, D.C. This incorporation by reference was approved by the Director of the Federal Register on November 8, 1982. This material is incorporated as it exists on the date of approval and a notice of any change in these materials will be published in the Federal Register.

2.3 Solvent Density. Determine the density of the solvent according to the procedure outlined in ASTM D 1475-60 (reapproved 1980). Make a total of three determinations for each coating. Report the density  $D_o$  as the arithmetic average of the three determinations.

**3. Calculations.**

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

$$W_o = \frac{M_{s1} + M_{cyl1} - M_{cyl2} - M_{d2}}{M_{cyl1} - M_{cyl2}}$$

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:

$$V_o = \frac{W_o \bar{D}_c}{D_o}$$

**4. Bibliography.**

4.1 Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475-60 (Reapproved 1980).

4.2 Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R. A., Radian Corporation. September 25, 1979. Gravure Ink Analysis.

4.3 Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979. Gravure Ink Analysis.

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METHOD 25 - DETERMINATION OF TOTAL GASEOUS NONMETHANE  
ORGANIC EMISSIONS AS CARBON

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the

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

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide ( $\text{CO}_2$ ) which is quantitatively collected in an evacuated vessel; then a portion of the  $\text{CO}_2$  is reduced to methane ( $\text{CH}_4$ ) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide ( $\text{CO}$ ),  $\text{CO}_2$  and  $\text{CH}_4$ ; the nonmethane organics (NMO) are oxidized to  $\text{CO}_2$ , reduced to  $\text{CH}_4$ , and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

## 2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems; an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst,



nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.2-mm OD (1/8-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within  $\pm 10$  percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0-900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO<sub>2</sub> concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect.

Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0-900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO<sub>2</sub> and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO<sub>2</sub>, and CH<sub>4</sub> from nonmethane organic compounds, (2) reducing the CO<sub>2</sub> to CH<sub>4</sub> and quantifying as CH<sub>4</sub>, and (3) oxidizing the nonmethane organic compounds to CO<sub>2</sub>, reducing the CO<sub>2</sub> to CH<sub>4</sub> and quantifying as CH<sub>4</sub>. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1).

Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3).

Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO<sub>2</sub>, and CH<sub>4</sub> from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5).

Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response ( $\pm 5\%$ ) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH<sub>4</sub>.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe(2). 10  $\mu$ l and 100  $\mu$ l liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

### 3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent  $O_2$  in  $N_2$ , containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than  $\pm 5$  percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal  $\text{CO}_2$  concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm  $\text{CH}_4$ , 2 percent  $\text{CO}_2$ , and 20 ppm  $\text{C}_3\text{H}_8$ , prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

#### 4. Procedure

##### 4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vacuum using a mercury U-tube manometer. Record this vacuum ( $P_{ti}$ ), the ambient temperature ( $T_{ti}$ ), and the barometric pressure ( $P_{bi}$ ) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse

the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

#### 4.1.3 Pretest Leak Check. A pretest leak check is required.

After the sampling train is assembled, record the tank vacuum as indicated by the vacuum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

#### 4.1.4 Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate ( $\pm 10$ percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter

setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and gauge vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.



4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum ( $P_t$ ); record the tank temperature ( $T_t$ ) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values,  $B_{ti}$  and  $B_{tf}$ , respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any  $\text{CO}_2$  which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR; when  $\text{CO}_2$  is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure ( $P_{tf}$ ), barometric pressure ( $P_{bf}$ ), and ambient temperature ( $T_{tf}$ ). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin.

From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnace (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure

( $P_f$ ) as well as the barometric pressure ( $P_{bv}$ ), ambient temperature ( $T_v$ ), and collection vessel volume ( $V_v$ ).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the  $CO_2$  and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensible organics as  $CO_2$  ( $C_{cm}$ ).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics ( $C_{tm}$ ).

## 5. Calibration and Operational Checks

Maintain a record of performance of each item.

### 5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for  $\text{CO}_2$ ; the carrier blank is acceptable if the  $\text{CO}_2$  concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cylinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions.

Analyze the collection vessel for CO<sub>2</sub>; the catalyst efficiency is acceptable if the CO<sub>2</sub> concentration is within  $\pm 5$  percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO<sub>2</sub> concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is  $100 \pm 10$  percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100  $\mu$ l hexane.

5.1.3.2 10  $\mu$ l hexane.

5.1.3.3 100  $\mu$ l toluene.

5.1.3.4 10  $\mu$ l toluene.

## 5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3. Make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within  $\pm 5$  percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than  $\pm 5$  percent. Record the overall mean of the propane response factor values as the NMO calibration response factor ( $RF_{NMO}$ ).

5.2.3 Reduction Catalyst Efficiency Check and CO<sub>2</sub> Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO<sub>2</sub> response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO<sub>2</sub> calibration gases (section 3.3.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the

response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within  $\pm 5$  percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than  $\pm 5$  percent. Additionally, the  $\text{CO}_2$  overall mean response factor must be within  $\pm 10$  percent of the NMO calibration response factor ( $\text{RF}_{\text{NMO}}$ ) calculated in section 5.2.2. Record the overall mean of the response factor values as the  $\text{CO}_2$  calibration response factor ( $\text{RF}_{\text{CO}_2}$ ).

5.2.4 NMO System Blank. For the high level  $\text{CO}_2$  calibration gas (section 3.3.3) record the NMO value measured during the  $\text{CO}_2$  calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer ( $B_a$ ) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within  $\pm 12$  percent of the expected value.

### 5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and  $\text{CO}_2$ . Inject triplicate samples of the high level  $\text{CO}_2$  calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within  $\pm 10$  percent of the  $\text{RF}_{\text{CO}_2}$  calculated during the initial performance test (section 5.2.2). Use the daily response factor ( $\text{DRF}_{\text{CO}_2}$ ) for analyzer calibration and the calculation of



measured  $\text{CO}_2$  concentrations in the collection vessel samples.

In addition, record the NMO blank value ( $B_a$ ); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within  $\pm 10$  percent of the  $\text{RF}_{\text{NMO}}$  calculated during the initial performance test (section 5.2.1). Use the daily response factor ( $\text{DRF}_{\text{NMO}}$ ) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect  $\text{CO}_2$  during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

## 6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

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

$$V_s = 0.386 V \left( \frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right)$$

6.2 Noncondensable Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[ \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right] \left[ \frac{1}{r} \sum_{j=1}^r C_{tmj} - B_a \right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386 \frac{V_v P_f}{V_s T_f} \left[ \frac{1}{q} \sum_{k=1}^q C_{cmk} - B_t \right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498 C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6 \frac{M}{L} \frac{V_v}{\rho} \frac{P_f}{T_f} \frac{C_{cm}}{N}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

Where:

- $B_a$  = Measured NMO blank value for NMO analyzer, ppm C
- $B_t$  = Measured  $CO_2$  blank value for condensate recovery and conditioning system carrier gas, ppm  $CO_2$ .
- $C$  = Total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.
- $C_c$  = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
- $C_{cm}$  = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm  $CO_2$ .
- $C_t$  = Calculated noncondensable organic concentration (sample tank) of the effluent, ppm C equivalent.
- $C_{tm}$  = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
- $L$  = Volume of liquid injected, microliters.
- $M$  = Molecular weight of the liquid injected, g/g-mole.
- $M_c$  = Total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.
- $N$  = Carbon number of the liquid compound injected ( $N = 7$  for toluene,  $N = 6$  for hexane).
- $P_f$  = Final pressure of the intermediate collection vessel, mm Hg absolute.
- $P_{ti}$  = Gas sample tank pressure prior to sampling, mm Hg absolute.

- $P_t$  = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.
- $P_{tf}$  = Final gas sample tank pressure after pressurizing, mm Hg absolute.
- $T_f$  = Final temperature of intermediate collection vessel, °K.
- $T_{ti}$  = Sample tank temperature prior to sampling, °K.
- $T_t$  = Sample tank temperature at completion of sampling, °K.
- $T_{tf}$  = Sample tank temperature after pressurizing, °K.
- $V$  = Sample tank volume, cm.
- $V_y$  = Intermediate collection vessel volume, cm.
- $V_s$  = Gas volume sampled, dscm.
- $n$  = Number of data points.
- $q$  = Total number of analyzer injections of intermediate collection vessel during analysis (where  $k$  = injection number, 1 . . .  $q$ ).
- $r$  = Total number of analyzer injections of sample tank during analysis (where  $j$  = injection number, 1 . . .  $r$ ).
- $x_i$  = Individual measurements.
- $\bar{X}$  = Mean value.
- $\rho$  = Density of liquid injected, g/cc.

## 7. Bibliography

7.1 Salo, Albert E., Samuel Witz, and Robert D. MacPhee.

Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A comparison of Infrared with Flame Ionization Detectors. Paper No. 75-33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15-20, 1975.) 14 p.

7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee.

Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74-190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9-13, 1974.) 25 p.

## METHOD 25

### ADDENDUM I. SYSTEM COMPONENTS

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as, to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. 3/8" OD X 14" inconel tubing packed with 8 inches of hopcalite\* oxidizing catalyst and operated at 800°C in a tube furnace. Note: A this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. 1/4" OD X 14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module; Byron Instruments, Raleigh, N.C.

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\* MSA registered trade mark.

4. Gas Chromatographic Separation Column. 1/8 inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min N<sub>2</sub> purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at -78°C (dry ice bath) to elute CO and CH<sub>4</sub>. After the CH<sub>4</sub> peak operate the column at 0°C to elute CO<sub>2</sub>. When the CO<sub>2</sub> is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100° C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note: The dry ice operating condition may be deleted if separation of CO and CH<sub>4</sub> is unimportant.

Note: Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the CO<sub>2</sub> concentration in the gas sample. When high levels of CO<sub>2</sub> are present, ethane and ethylene will elute under the tail of the CO<sub>2</sub> peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.



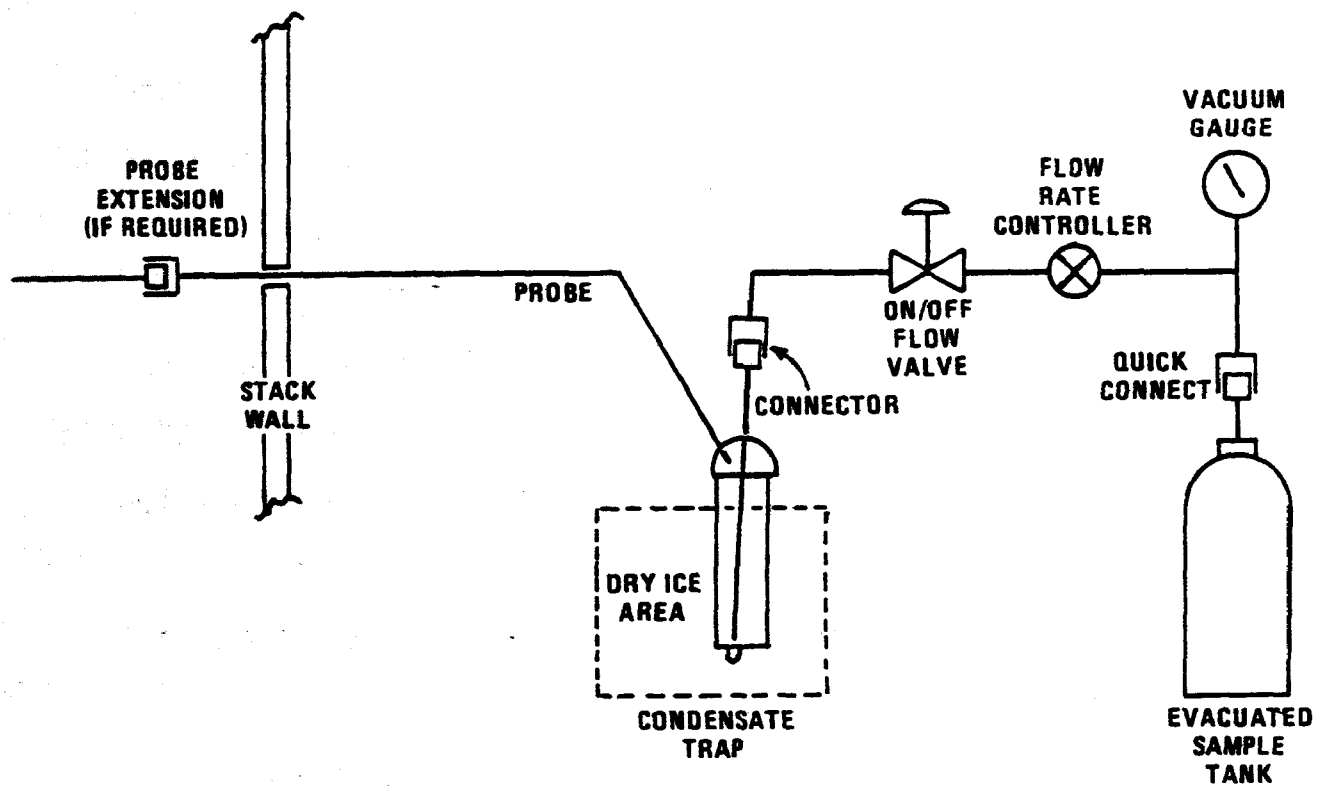


Figure 1. Sampling apparatus.

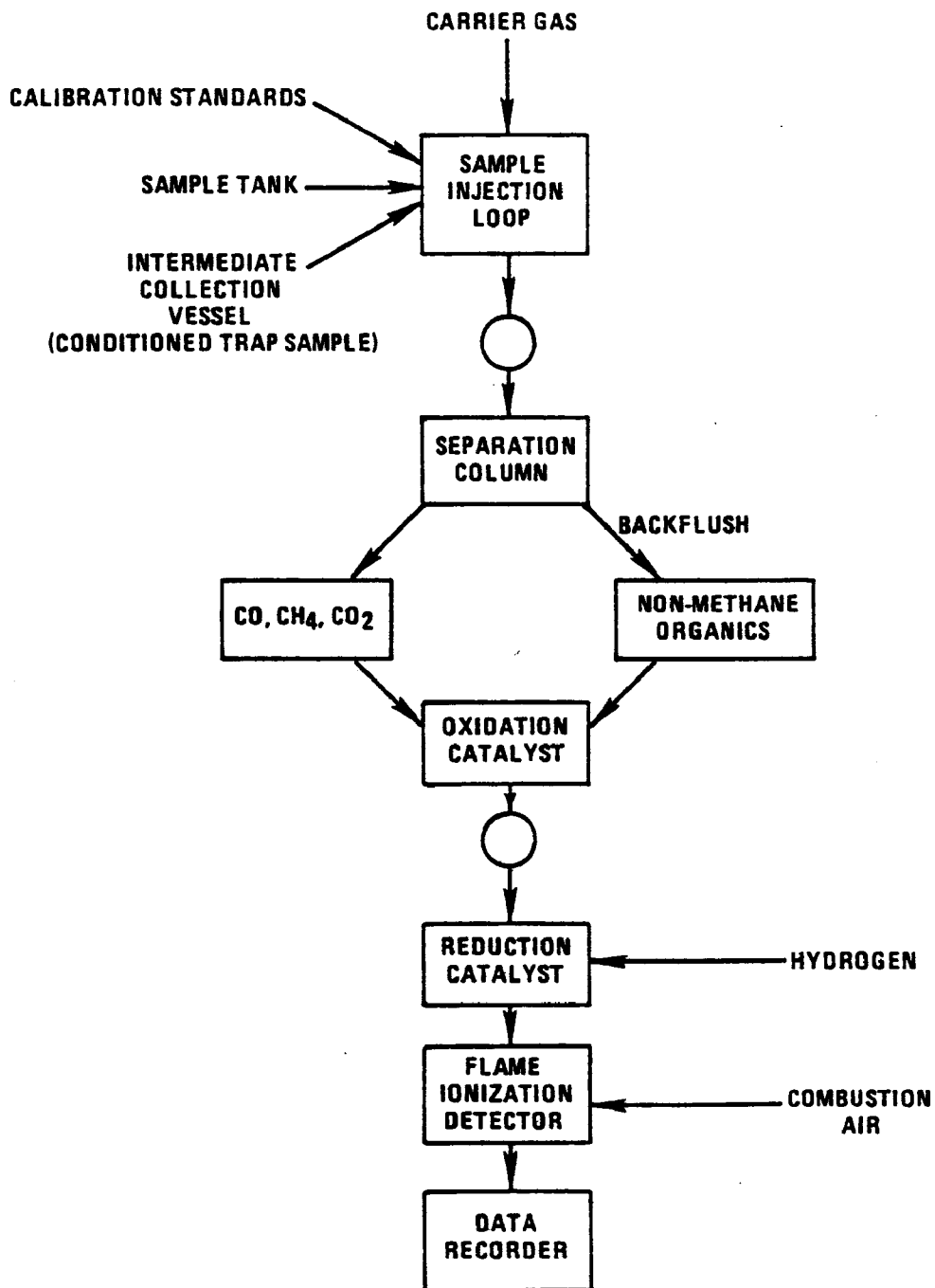


Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

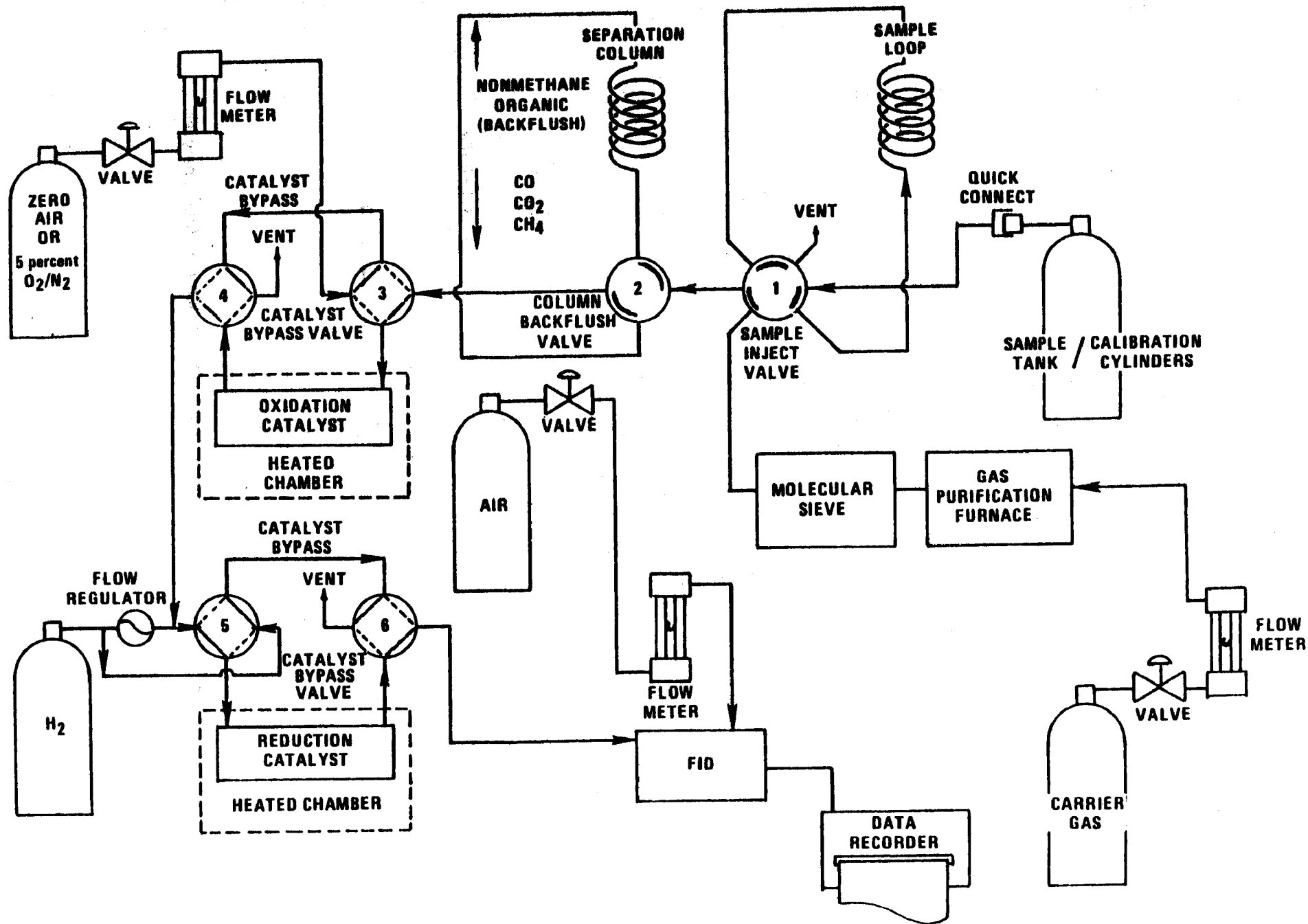


Figure 3. Nonmethane organic (NMO) analyzer.

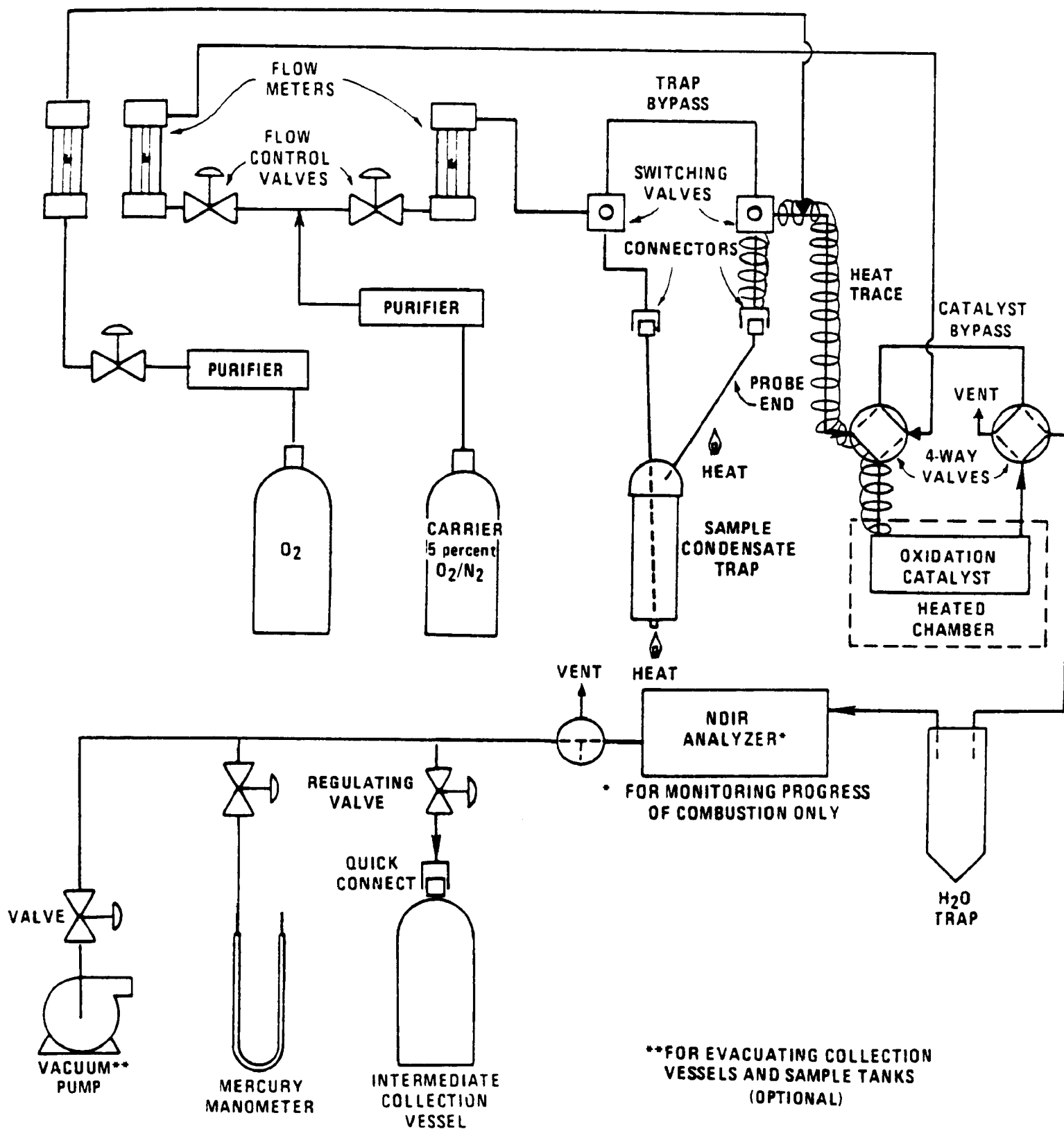
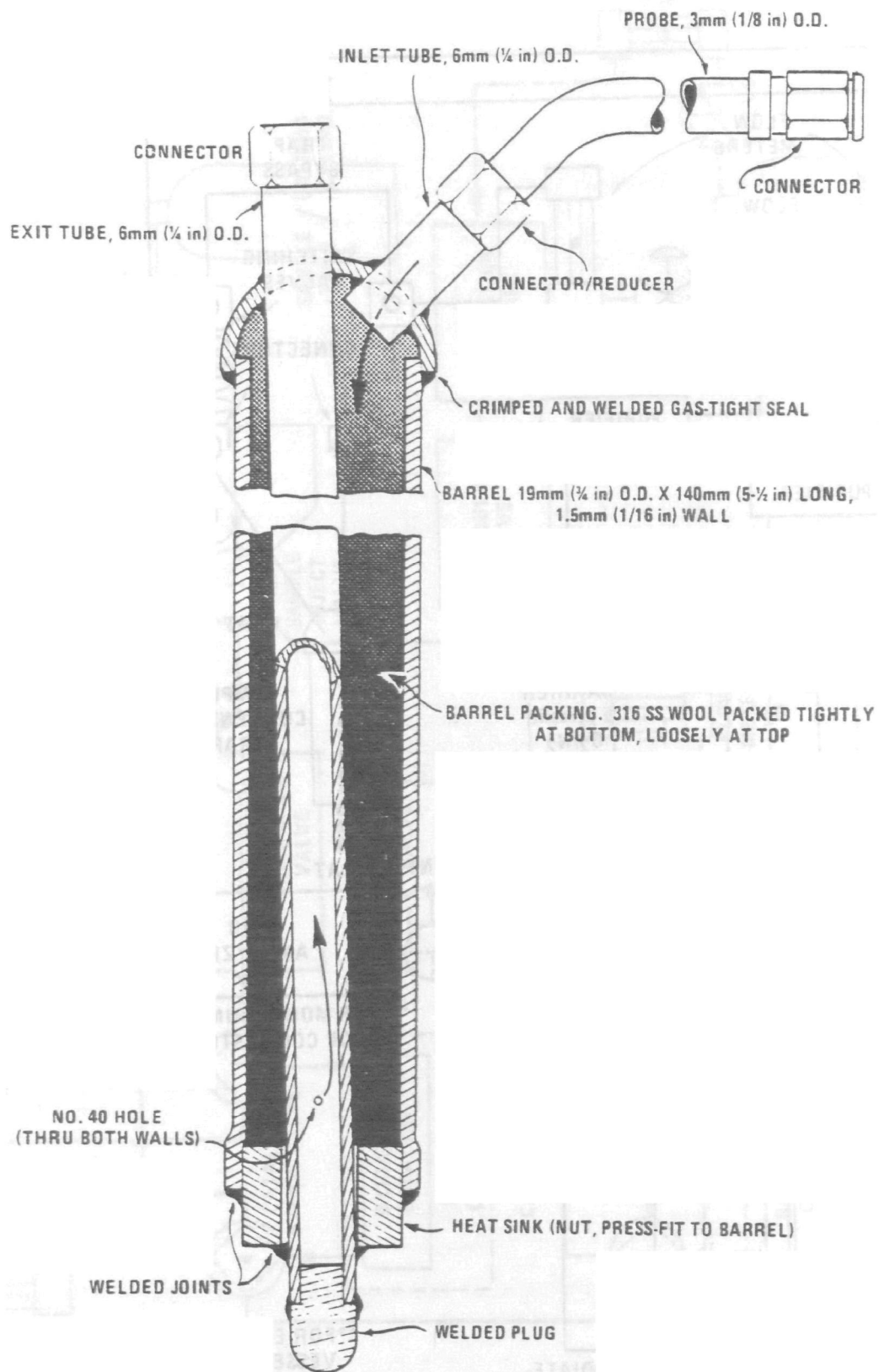


Figure 4. Condensate recovery and conditioning apparatus.



**MATERIAL: TYPE 316 STAINLESS STEEL**

Figure 5. Condensate trap<sup>2</sup>.

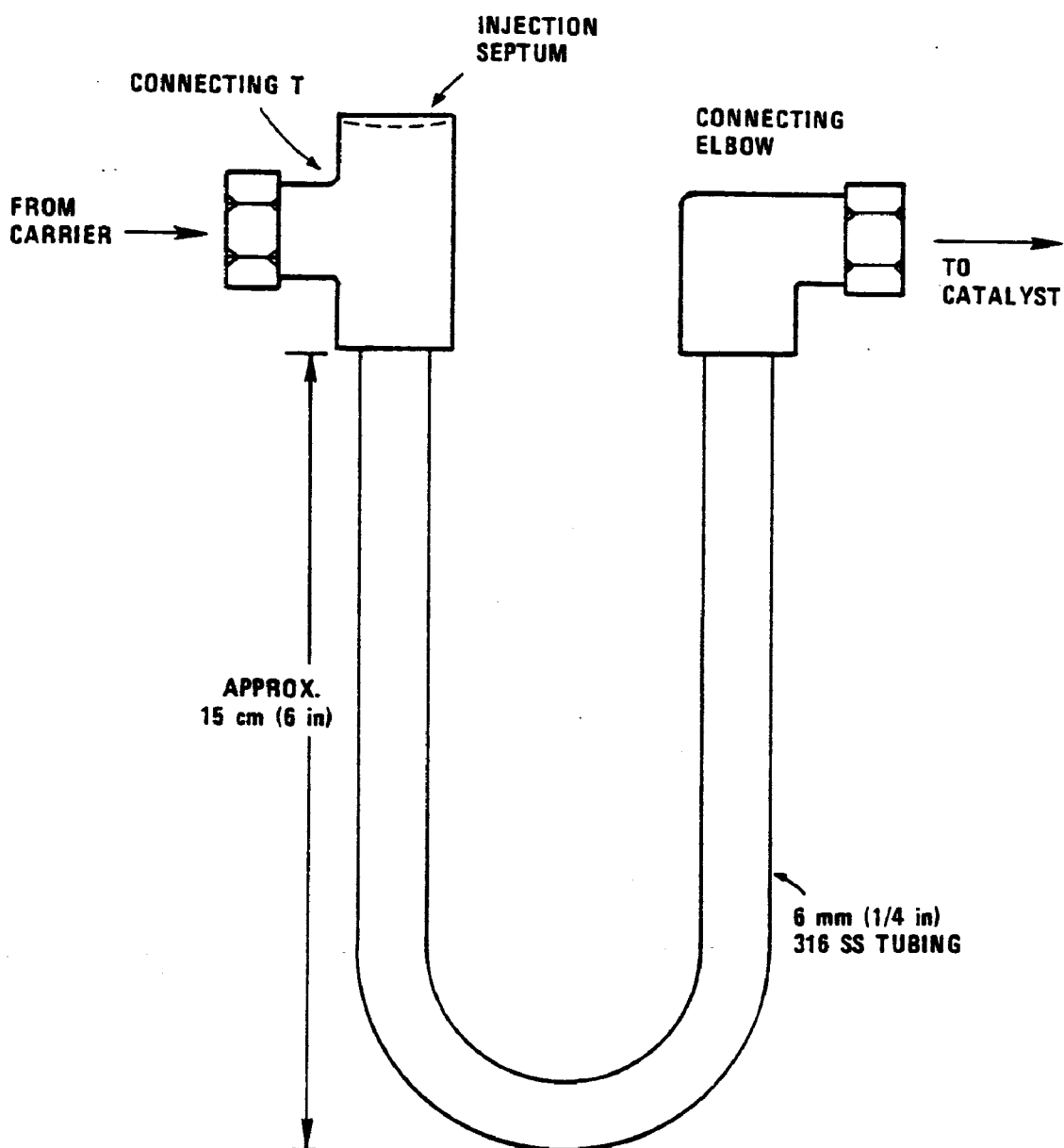


Figure 6. Liquid sample injection unit.

FACILITY \_\_\_\_\_ SAMPLE LOCATION \_\_\_\_\_  
LOCATION \_\_\_\_\_ OPERATOR \_\_\_\_\_  
DATE \_\_\_\_\_ RUN NUMBER \_\_\_\_\_  
TANK NUMBER \_\_\_\_\_ TRAP NUMBER \_\_\_\_\_ SAMPLE ID NUMBER \_\_\_\_\_

TANK VACUUM,		BAROMETRIC PRESSURE,	AMBIENT TEMPERATURE,
mm Hg	cm Hg	mm Hg	°C
PRETEST (MANOMETER) _____ (GAUGE) _____		_____	_____
POST TEST (MANOMETER) _____ (GAUGE) _____		_____	_____

LEAK RATE cm Hg / 10 min

---

PRETEST \_\_\_\_\_

POST TEST \_\_\_\_\_

[illegible]

25-34

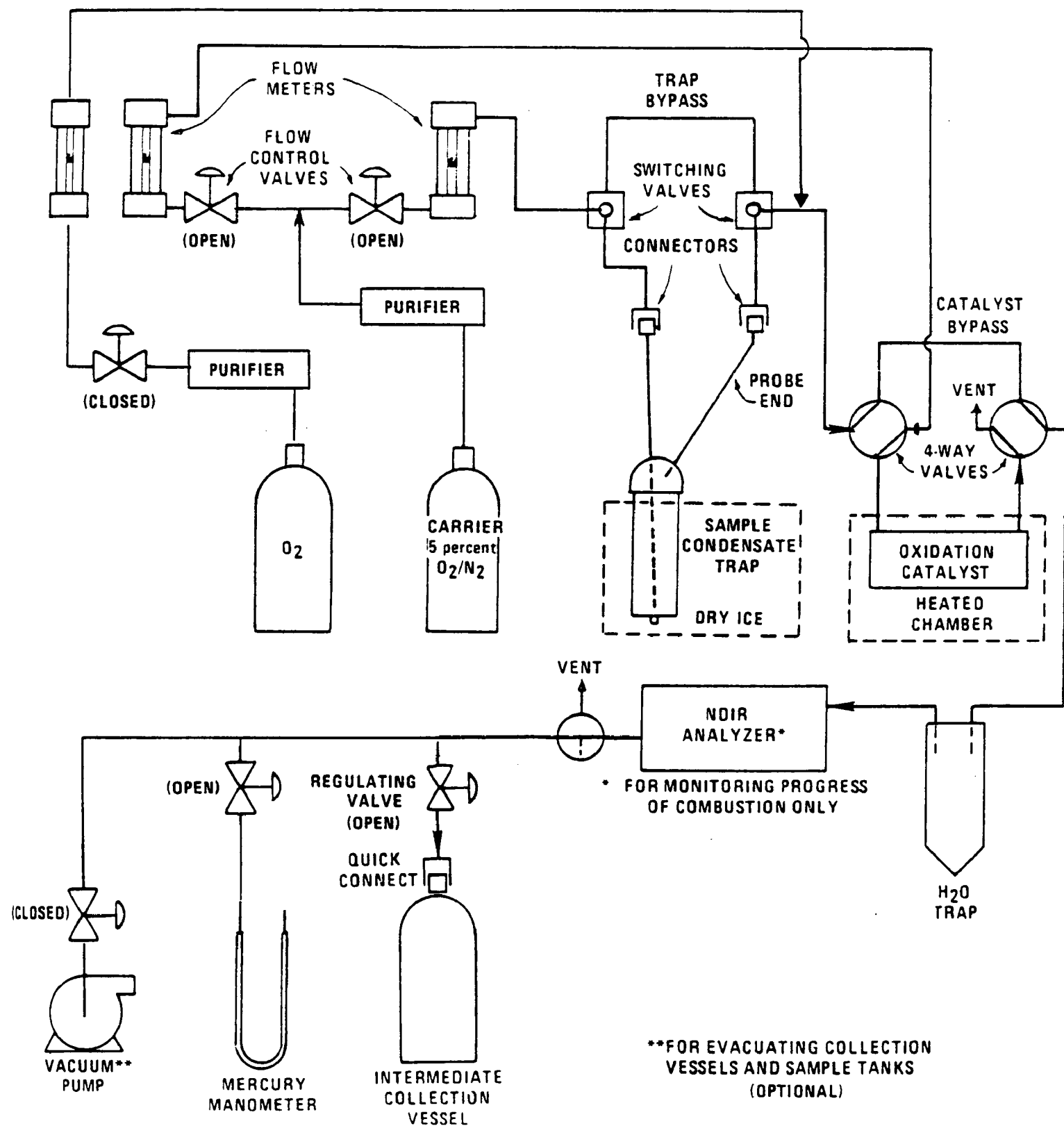


Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.



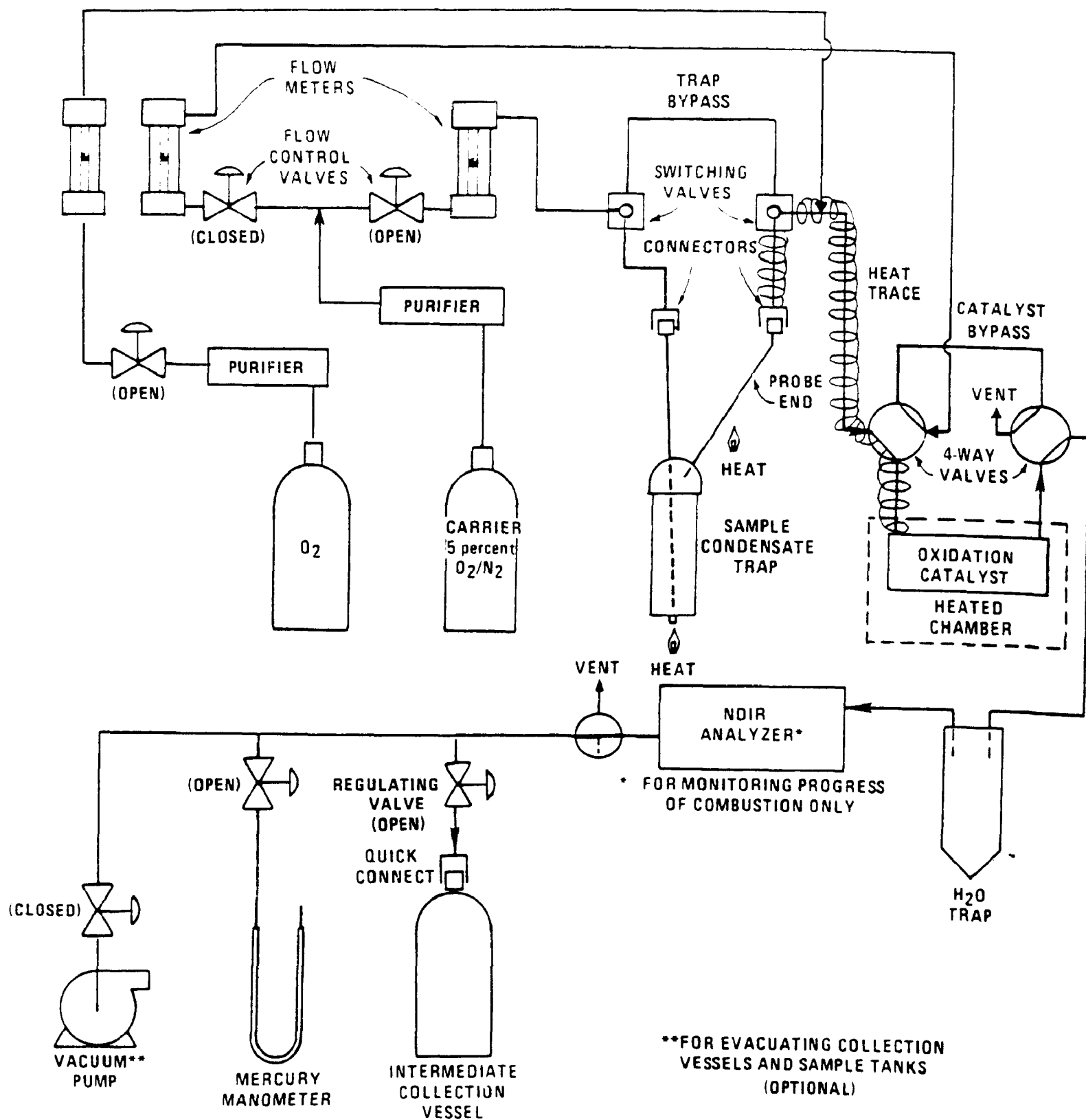


Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

**1.2 Principle.** An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide ( $\text{CO}_2$ ) which is quantitatively collected in an evacuated vessel; then a portion of the  $\text{CO}_2$  is reduced to methane ( $\text{CH}_4$ ) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO),  $\text{CO}_2$ , and  $\text{CH}_4$ ; the nonmethane organics (NMO) are oxidized to

#### **Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon**

##### **1. Applicability and Principle**

**1.1 Applicability.** This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO.

CO<sub>2</sub> reduced to CH<sub>4</sub> and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

## 2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems: an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TCNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.2-mm OD (1/8-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within  $\pm 10$  percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0-800 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using

both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak-proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO<sub>2</sub> concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect. Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0-800 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO<sub>2</sub> and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO<sub>2</sub>, and CH<sub>4</sub> from nonmethane organic compounds, (2) reducing the CO<sub>2</sub> to CH<sub>4</sub> and quantifying as CH<sub>4</sub>, and (3) oxidizing the nonmethane organic compounds to CO<sub>2</sub>, reducing the CO<sub>2</sub> to CH<sub>4</sub>, and quantifying as CH<sub>4</sub>. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO<sub>2</sub>, and CH<sub>4</sub> from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response ( $\pm 5\%$ ) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH<sub>4</sub>.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe (2). 10  $\mu$ l and 100  $\mu$ l liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

## 3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O<sub>2</sub> in N<sub>2</sub>, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than  $\pm 5$  percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO<sub>2</sub> concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH<sub>4</sub>, 2 percent CO<sub>2</sub>, and 20 ppm C<sub>2</sub>H<sub>6</sub>, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

#### 4. Procedure

##### 4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vacuum using a mercury U-tube manometer. Record this vacuum ( $P_u$ ), the ambient temperature ( $T_u$ ), and the barometric pressure ( $P_b$ ) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3. Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vacuum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4. Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate ( $\pm 10$  percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off

valve and record the final sample time and gauge vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum ( $P_t$ ); record the tank temperature ( $T_t$ ) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values,  $B_i$  and  $B_f$ , respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The

first step in analysis is to purge the condensate trap of any  $CO_2$  which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap. Immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR when  $CO_2$  is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure ( $P_u$ ), barometric pressure ( $P_b$ ), and ambient temperature ( $T_u$ ). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnace (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm

Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure ( $P_i$ ) as well as the barometric pressure ( $P_b$ ), ambient temperature ( $T_a$ ), and collection vessel volume ( $V_c$ ).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the  $CO_2$  and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensable organics as  $CO_2$  ( $C_{con}$ ).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics ( $C_{nm}$ ).

### 5. Calibration and Operational Checks

Maintain a record of performance of each item.

#### 5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for  $CO_2$ ; the carrier blank is acceptable if the  $CO_2$  concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cylinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the

intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Analyze the collection vessel for  $CO_2$ ; the catalyst efficiency is acceptable if the  $CO_2$  concentration is within  $\pm 5$  percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the  $CO_2$  concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is  $100 \pm 10$  percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100  $\mu$ l hexane.

5.1.3.2 10  $\mu$ l hexane.

5.1.3.3 100  $\mu$ l toluene.

5.1.3.4 10  $\mu$ l toluene.

#### 5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3. make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within  $\pm 5$  percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than  $\pm 5$  percent. Record the overall mean of the propane response factor values as the NMO calibration response factor ( $RF_{NMO}$ ).

5.2.3 Reduction Catalyst Efficiency Check and  $CO_2$  Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a  $CO_2$  response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the  $CO_2$  calibration gases (section 3.3.3). Calculate the average response factor

(area/ppm) for each calibration gas, as well as the overall mean of the response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within  $\pm 5$  percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than  $\pm 5$  percent. Additionally, the  $CO_2$  overall mean response factor must be within  $\pm 10$  percent of the NMO calibration response factor ( $RF_{NMO}$ ) calculated in section 5.2.2. Record the overall mean of the response factor values as the  $CO_2$  calibration response factor ( $RF_{CO_2}$ ).

5.2.4 NMO System Blank. For the high level  $CO_2$  calibration gas (section 3.3.3) record the NMO value measured during the  $CO_2$  calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer ( $B_A$ ) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within  $\pm 12$  percent of the expected value.

#### 5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and  $CO_2$ . Inject triplicate samples of the high level  $CO_2$  calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within  $\pm 10$  percent of the  $RF_{CO_2}$  calculated during the initial performance test (section 5.2.2). Use the daily response factor ( $DRF_{CO_2}$ ) for analyzer calibration and the calculation of measured  $CO_2$  concentrations in the collection vessel samples. In addition, record the NMO blank value ( $B_A$ ); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within  $\pm 10$  percent of the  $RF_{NMO}$  calculated during the initial performance test (section 5.2.1). Use the daily response factor ( $DRF_{NMO}$ ) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect  $CO_2$  during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

## 6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

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

$$V_s = 0.386 V \left( \frac{P_t}{T_t} - \frac{P_{t1}}{T_{t1}} \right)$$

6.2 Noncondensable Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[ \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{t1}}{T_{t1}}} \right] \left[ \frac{1}{r} \sum_{j=1}^r C_{tmj} - B_a \right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386 \frac{V_v P_f}{V_s T_f} \left[ \frac{1}{q} \sum_{k=1}^q C_{cmk} - B_t \right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498 C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6 \frac{M}{L} \frac{V_v}{D} \frac{P_f}{T_f} \frac{C_{cm}}{N}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

## Where:

- $B_a$  = Measured NMO blank value for NMO analyzer, ppm C.
- $B_c$  = Measured  $CO_2$  blank value for condensate recovery and conditioning system carrier gas, ppm  $CO_2$ .
- $C$  = total gaseous nonmethane organic (TCNMO) concentration of the effluent, ppm C equivalent.
- $C_c$  = Calculated condensable organic (condensate trap) concentration of the effluent, ppm C equivalent.
- $C_{cm}$  = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm  $CO_2$ .
- $C_t$  = Calculated noncondensable organic concentration (sample tank) of the effluent, ppm C equivalent.
- $C_{tm}$  = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
- $L$  = Volume of liquid injected, microliters.
- $M$  = Molecular weight of the liquid injected, g/g.mole.
- $M_t$  = total gaseous non-methane organic (TCNMO) mass concentration of the effluent, mg C/dscm.
- $N$  = Carbon number of the liquid compound injected ( $N=7$  for toluene,  $N=6$  for hexane).
- $P_i$  = Final pressure of the intermediate collection vessel, mm Hg absolute.
- $P_u$  = Gas sample tank pressure prior to sampling, mm Hg absolute.
- $P_s$  = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.
- $P_{su}$  = Final gas sample tank pressure after pressurizing, mm Hg absolute.
- $T_i$  = Final temperature of intermediate collection vessel, °K.
- $T_u$  = Sample tank temperature prior to sampling, °K.
- $T_c$  = Sample tank temperature at completion of sampling, °K.
- $T_{su}$  = Sample tank temperature after pressurizing, °K.
- $V$  = Sample tank volume, cm.
- $V_i$  = Intermediate collection vessel volume, cm.
- $V_s$  = Gas volume sampled, dscm.
- $n$  = Number of data points.
- $q$  = Total number of analyzer injections of intermediate collection vessel during analysis (where  $k$  = injection number, 1 to  $q$ ).
- $r$  = Total number of analyzer injections of sample tank during analysis (where  $i$  = injection number, 1 to  $r$ ).
- $x_i$  = Individual measurements.
- $\bar{X}$  = Mean value.
- $\rho$  = Density of liquid injected, g/cc.

## 7. Bibliography

7.1 Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75-33.2 (Presented at the 66th Annual Meeting of the Air Pollution Control Association, Boston, MA, June 15-20, 1975.) 14 p.

7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74-190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, CO, June 9-13, 1974.) 25 p.

## Method 25

## Addendum I. System Components

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst.  $\frac{1}{4}$ " OD  $\times$  14" inconel tubing packed with 8 inches of hopcalite\* oxidizing catalyst and operated at 800°C in a tube furnace. Note: At this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst.  $\frac{1}{4}$ " OD  $\times$  14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module: Byron Instruments, Raleigh, N.C.

4. Gas Chromatographic Separation Column.  $\frac{1}{8}$  inch OD stainless steel packed with 3 feet of 10 percent methyl silicone. Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min  $N_2$  purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at -78°C (dry ice bath) to elute CO and  $CH_4$ . After the  $CH_4$  peak operate the column at 0°C to elute  $CO_2$ . When the  $CO_2$  is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100°C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note.—The dry ice operating condition may be deleted if separation of CO and  $CH_4$  is unimportant.

Note.—Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the  $CO_2$  concentration in the gas sample. When high levels of  $CO_2$  are present, ethane and ethylene will elute under the tail of the  $CO_2$  peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

BILLING CODE 6550-01-M

\*MSA registered trademark

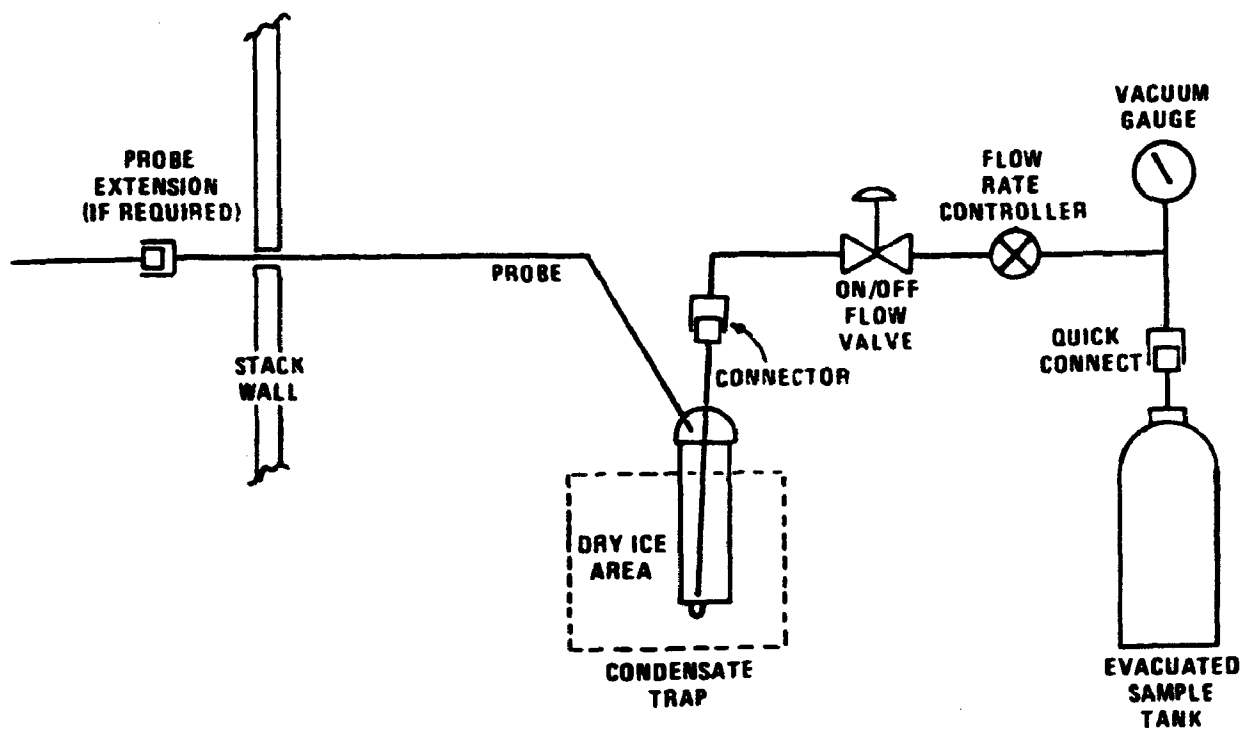


Figure 1. Sampling apparatus.



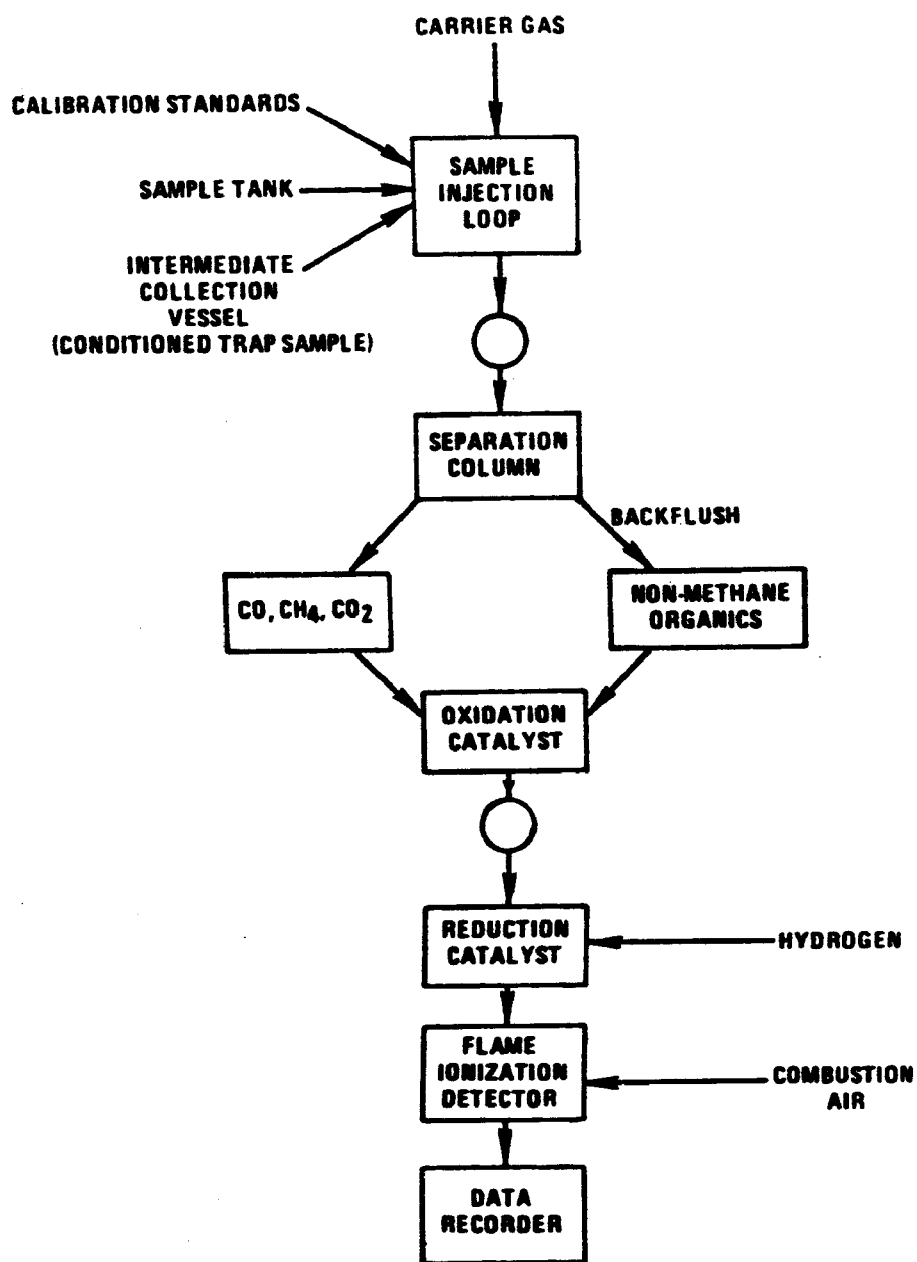


Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

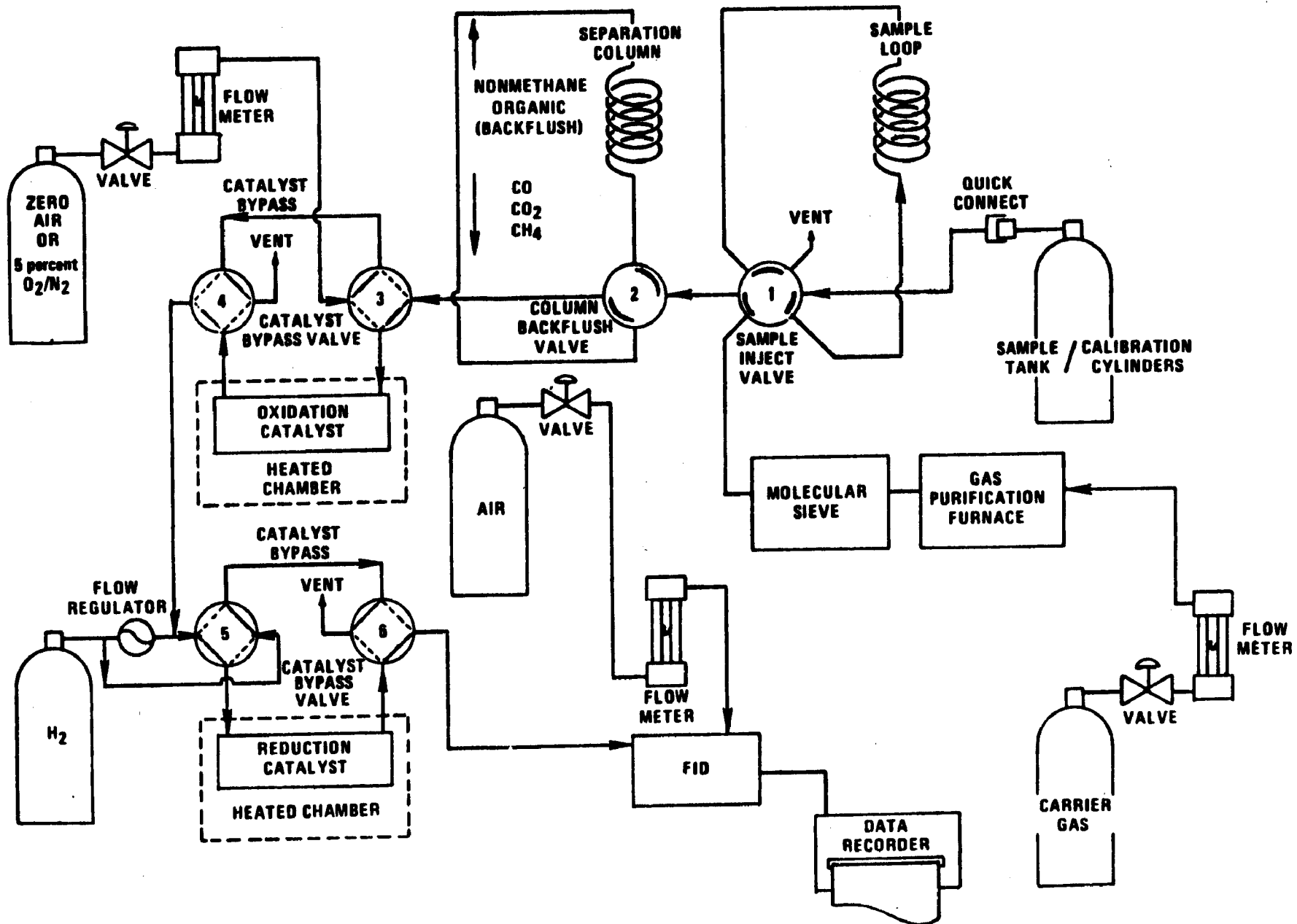


Figure 3. Nonmethane organic (NMO) analyzer.

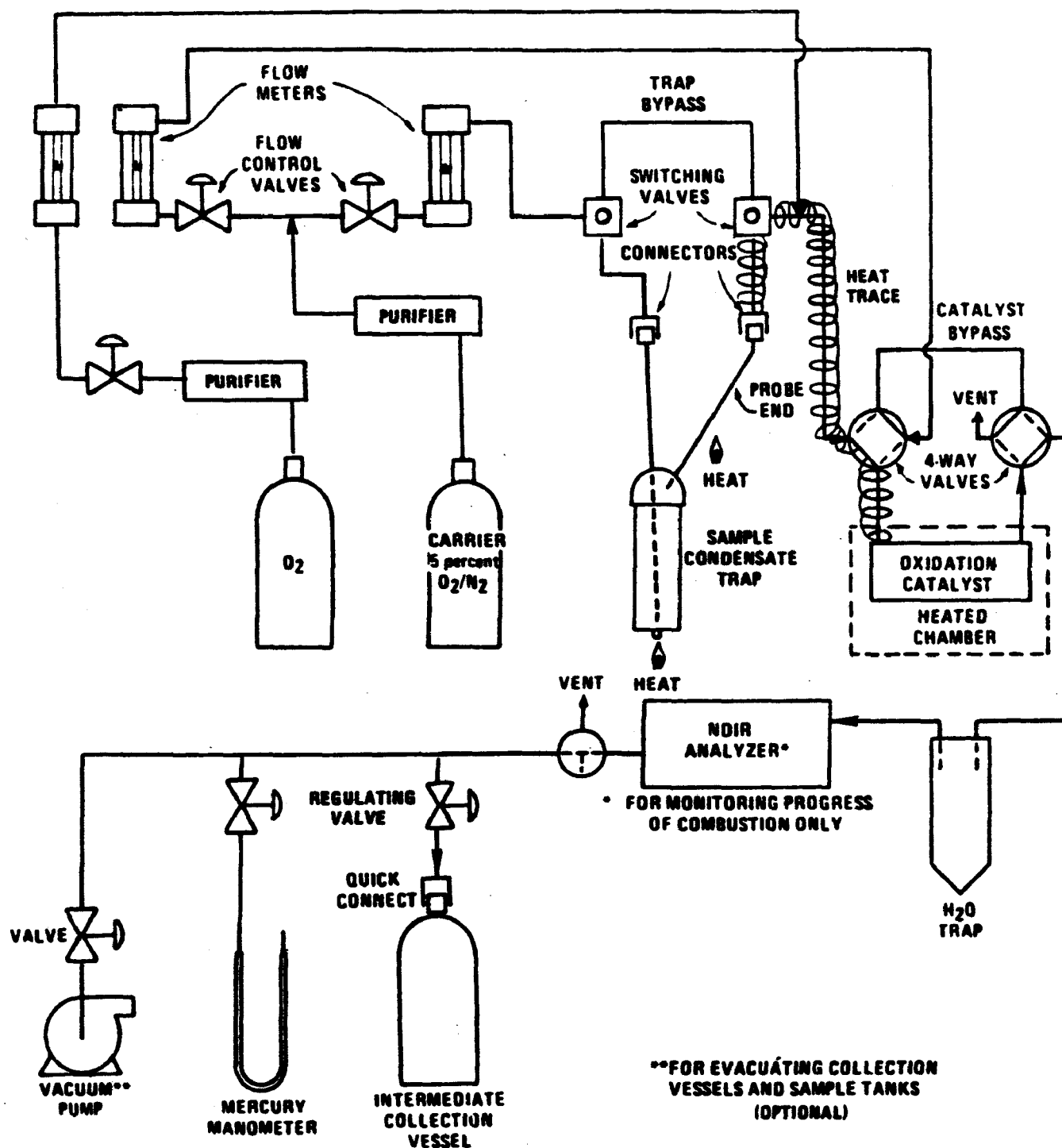
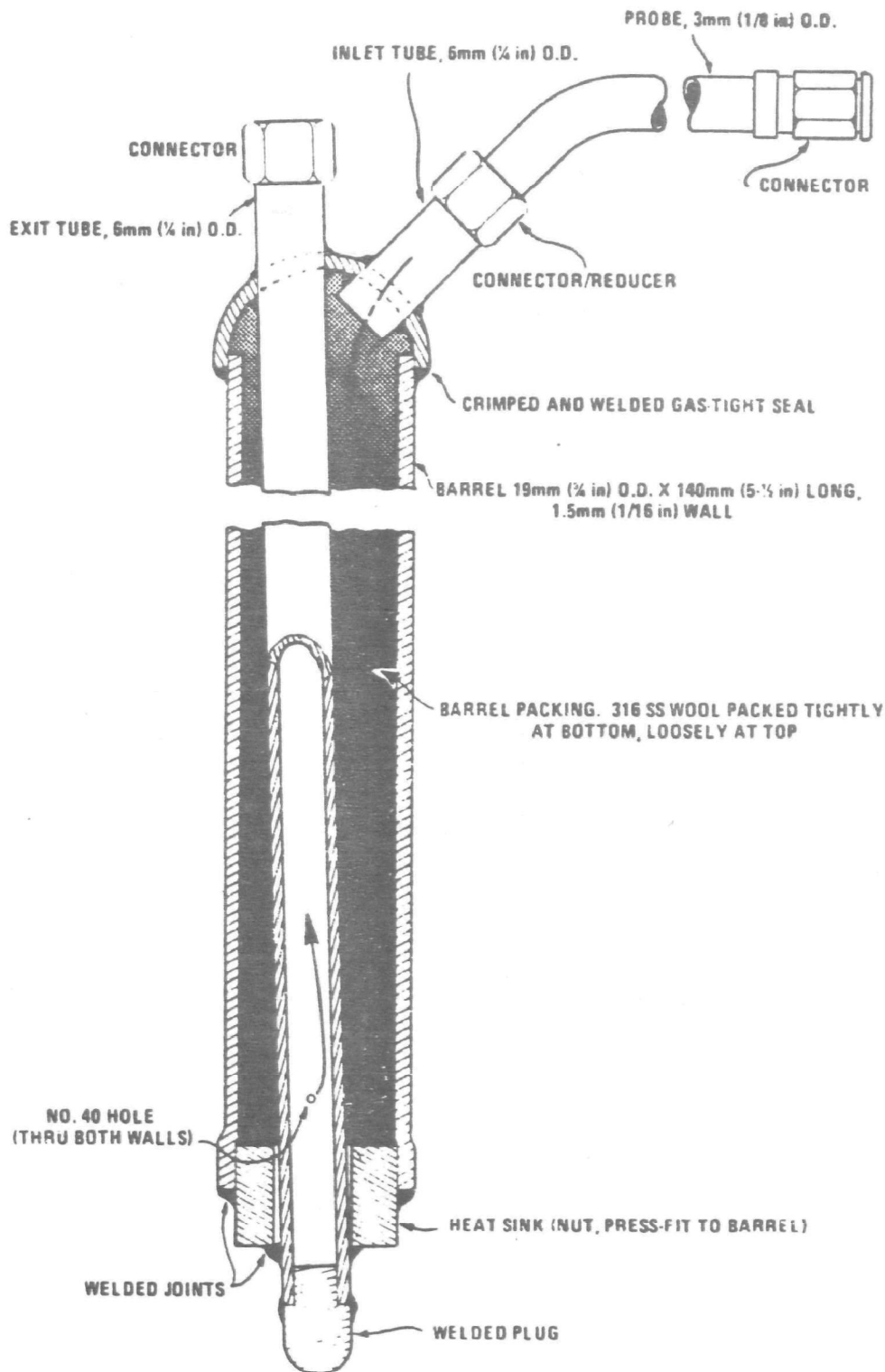


Figure 4. Condensate recovery and conditioning apparatus.



MATERIAL: TYPE 316 STAINLESS STEEL

Figure 5 Condensate trap<sup>2</sup>

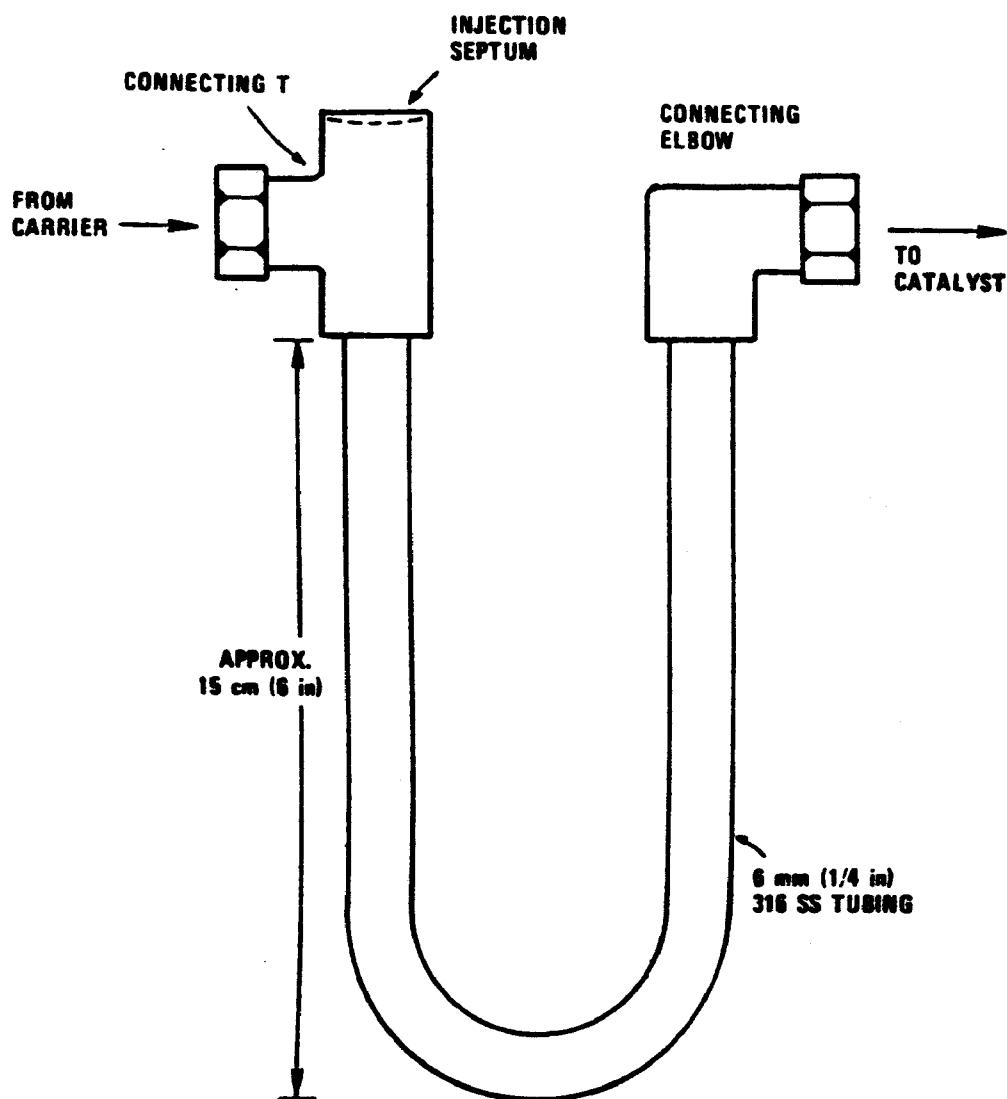


Figure 6. Liquid sample injection unit.

[illegible]

25-49

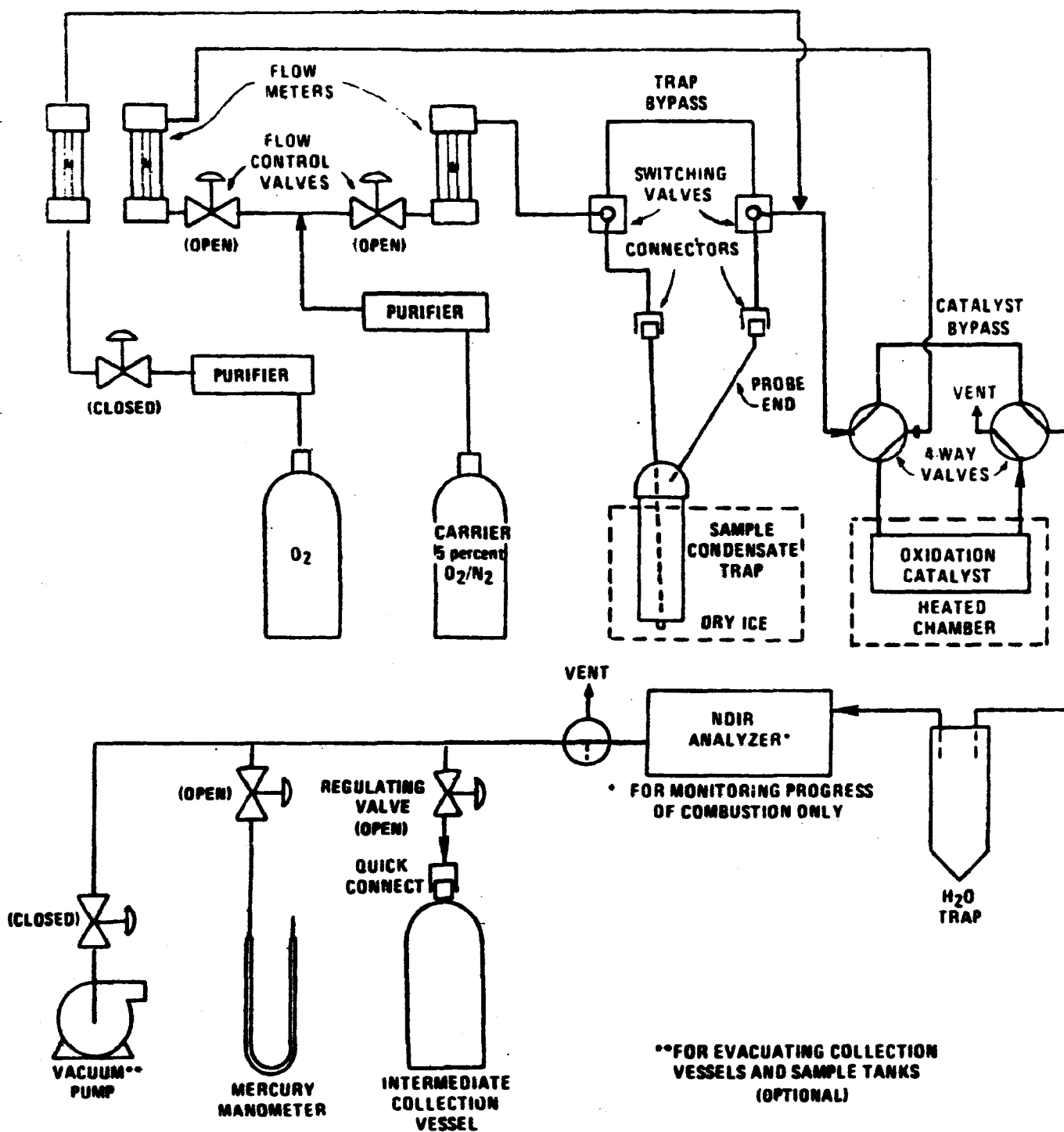


Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

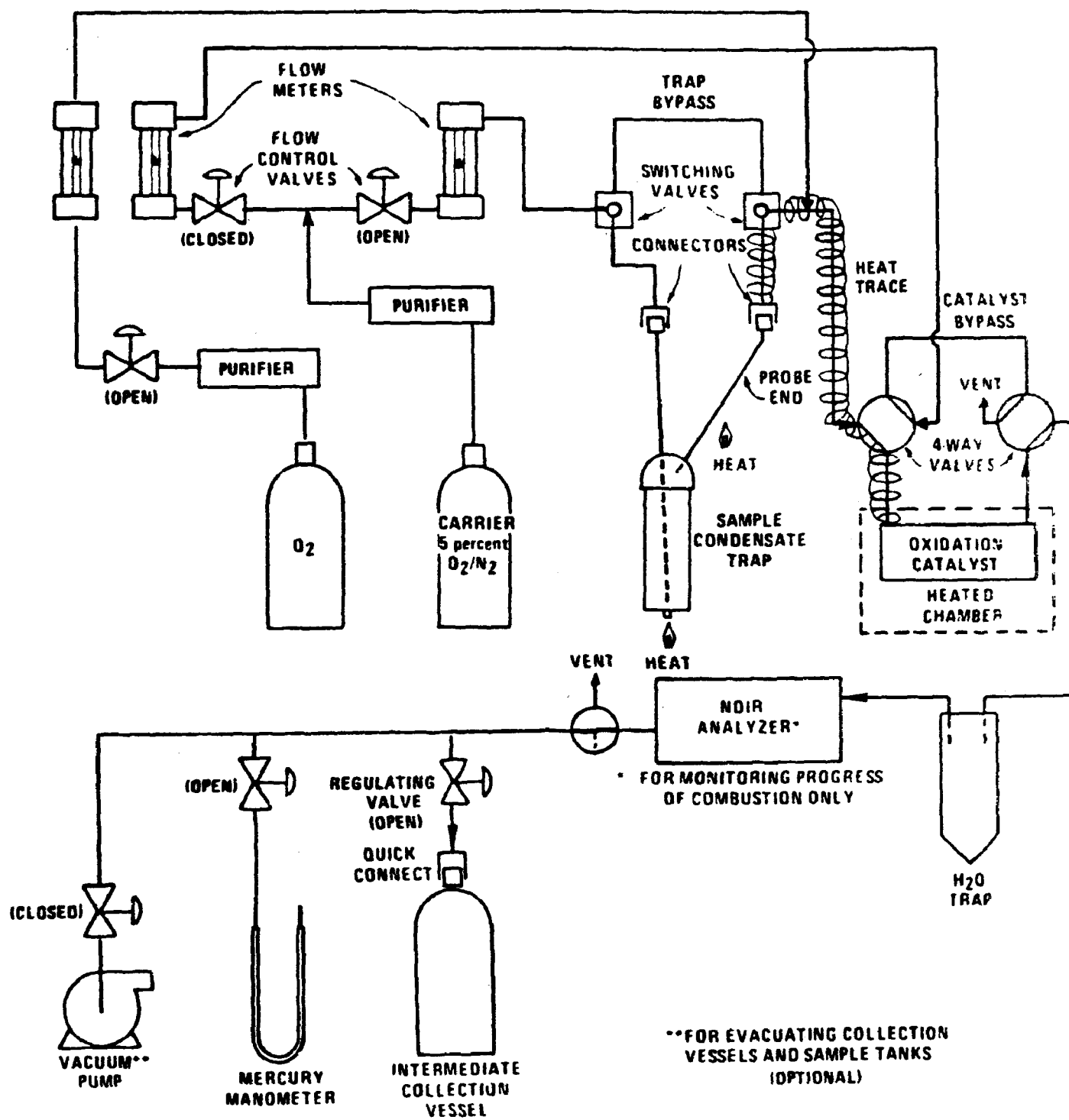


Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.



METHOD 25A - DETERMINATION OF TOTAL GASEOUS ORGANIC  
CONCENTRATION USING A FLAME IONIZATION ANALYZER

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. Definitions

2.1 Measurement System. The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 Organic Analyzer. That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in

the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

2.4 Zero Drift. The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 Calibration Drift. The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.6 Response Time. The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

### 3. Apparatus

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:

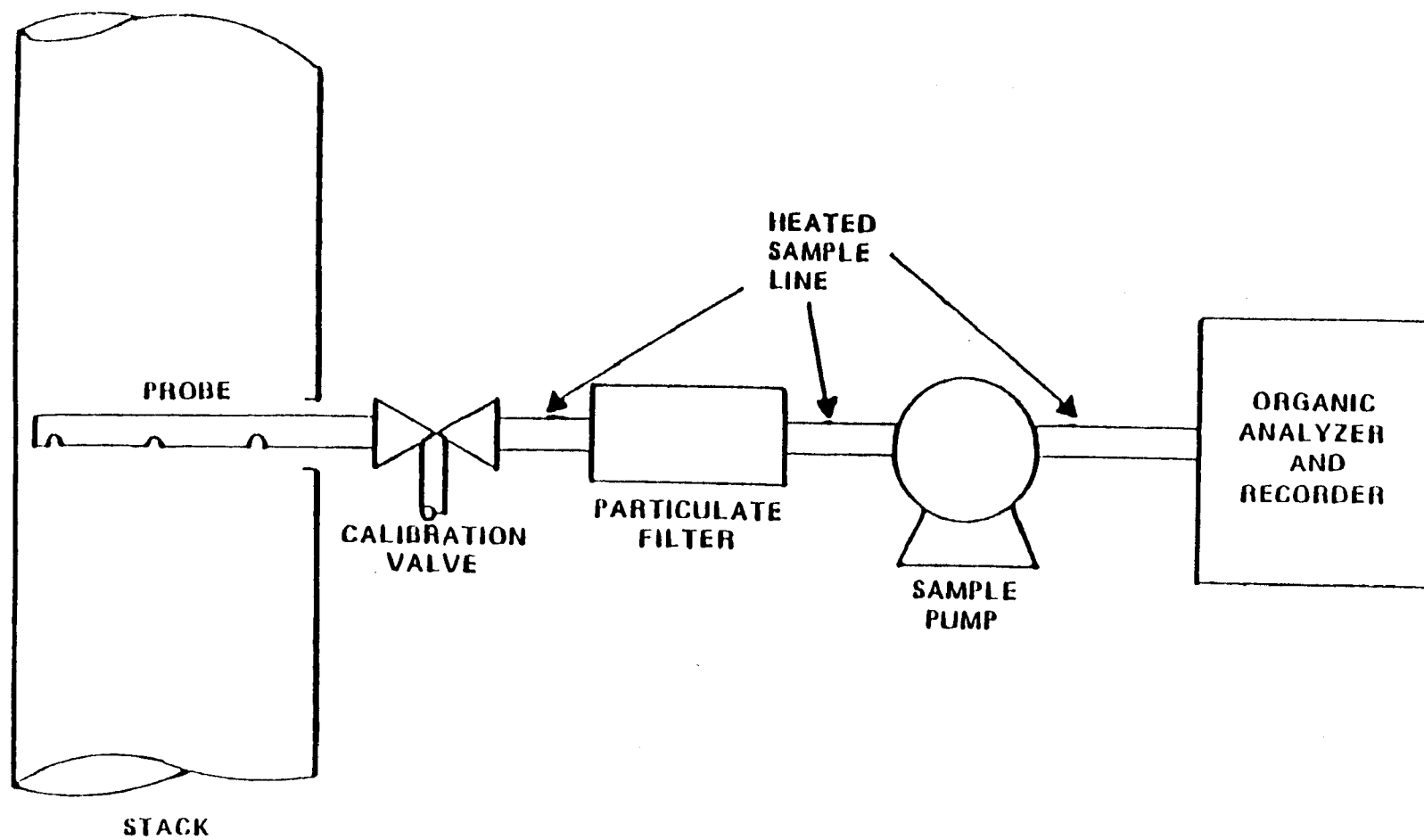


Figure 25A-1. Organic Concentration Measurement System.

3.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 Sample Line. Stainless steel or Teflon\* tubing to transport the sample gas to the analyzers. The sample line should be heated, if necessary, to prevent condensation in the line.

3.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

3.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

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\*Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

#### 4. Calibration and Other Gases

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than  $\pm 2$  percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

4.1 Fuel. A 40 percent  $H_2$ /60 percent He or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value..

4.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

## 5. Measurement System Performance Specifications

5.1 Zero Drift. Less than  $\pm 3$  percent of the span value.

5.2 Calibration Drift. Less than  $\pm 3$  percent of the span value.

5.3 Calibration Error. Less than  $\pm 5$  percent of the calibration gas value.

## 6. Pretest Preparations

6.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters (whichever is less) upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics (>1.0 percent by volume as propane) modifications to most commonly available

analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

6.4 Calibration Error Test. Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level-responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

## 7. Emission Measurement Test Procedure

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

## 8. Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.



If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_{\text{meas}}$$

Eq. 25A-1

Where:

$C_c$  = Organic concentration as carbon, ppmv.

$C_{\text{meas}}$  = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor,

K = 2 for ethane.

K = 3 for propane.

K = 4 for butane.

K = Appropriate response factor for other organic calibration gases.

## 9. Bibliography

### 9.1 Measurement of Volatile Organic Compounds - Guideline Series.

U.S. Environmental Protection Agency. Research Triangle Park, N.C.

Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

9.2 Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, N.C. June 1978.

9.3 Gasoline Vapor Emission Laboratory Evaluation - Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, N.C. EMB Report No. 75-GAS-6. August 1975.

equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

**2.1.1 Sample Interface.** That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

**2.1.2 Organic Analyzer.** That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

**2.2 Span Value.** The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

**2.3 Calibration Gas.** A known concentration of a gas in an appropriate diluent gas.

**2.4 Zero Drift.** The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

**2.5 Calibration Drift.** The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

**2.6 Response Time.** The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

**2.7 Calibration Error.** The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

### 3. Apparatus.

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:

**3.1 Organic Concentration Analyzer.** A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

**3.2 Sample Probe.** Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

**3.3 Sample Line.** Stainless steel or Teflon\* tubing to transport the sample gas to the analyzer. The sample line should be heated, if necessary, to prevent condensation in the line.

**3.4 Calibration Valve Assembly.** A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

**3.5 Particulate Filter.** An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

**3.6 Recorder.** A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

### 4. Calibration and Other Gases.

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than #2 percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

**4.1 Fuel.** A 40 percent  $H_2$ /60 percent He or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

**4.2 Zero Gas.** High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon

\* Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

## Method 25A—Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

### 1. Applicability and Principle.

**1.1 Applicability.** This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

**1.2 Principle.** A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

### 2. Definitions.

**2.1 Measurement System.** The total

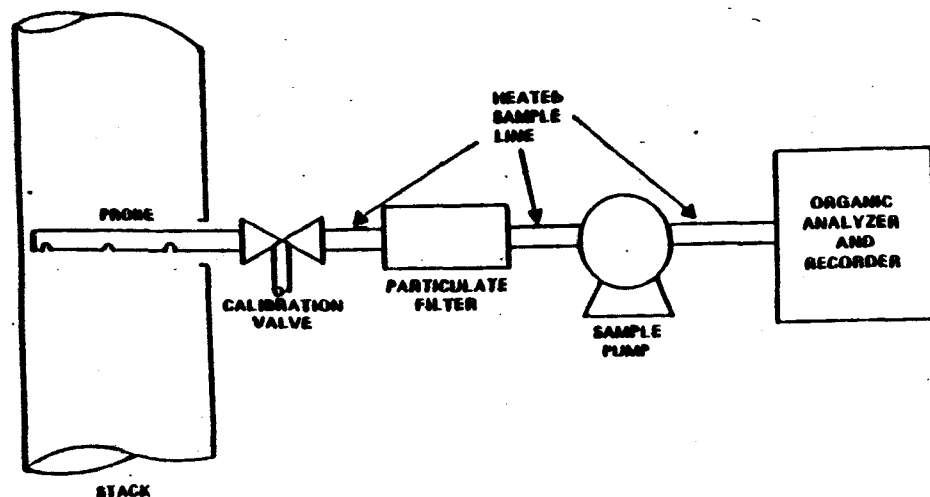


Figure 25A-1. Organic Concentration Measurement System.

equivalent) or less than 0.1 percent of the span value, whichever is greater.

**4.3 Low-level Calibration Gas.** An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

**4.4 Mid-level Calibration Gas.** An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

**4.5 High-level Calibration Gas.** An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

#### 5. Measurement System Performance Specifications.

**5.1 Zero Drift.** Less than  $\pm 3$  percent of the span value.

**5.2 Calibration Drift.** Less than  $\pm 3$  percent of span value.

**5.3 Calibration Error.** Less than  $\pm 5$  percent of the calibration gas value.

#### 6. Pretest Preparations.

**6.1 Selection of Sampling Site.** The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters (whichever is less) upstream of the gas discharge to the atmosphere.

**6.2 Location of Sample Probe.** Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

**6.3 Measurement System Preparation.** Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics ( $> 1.0$  percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

**6.4 Calibration Error Test.** Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and

before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

**6.5 Response Time Test.** Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

#### 7. Emission Measurement Test

**7.1 Organic Measurement.** Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

**7.2 Drift Determination.** Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

#### 8. Organic Concentration Calculations.

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_m$$

Eq. 25A-1

Where:

$C_c$  = Organic concentration as carbon, ppmv.

$C_m$  = Organic concentration as measured, ppmv.

$K$  = Carbon equivalent correction factor.

$K = 2$  for ethane.

$K = 3$  for propane.

$K = 4$  for butane.

$K$  = Appropriate response factor for other organic calibration gases.

#### 9. Bibliography.

9.1 Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

9.2 Traceability Protocol for Establishing True Concentrations of Gases Used for

**3.1 Organic Concentration Analyzer.** A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

**3.2 Sample Probe.** Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

**3.3 Sample Line.** Stainless steel or Teflon<sup>\*</sup> tubing to transport the sample gas to the analyzer. The sample line should be heated, if necessary, to prevent condensation in the line.

**3.4 Calibration Valve Assembly.** A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

**3.5 Particulate Filter.** An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

**3.6 Recorder.** A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

#### 4. Calibration and Other Gases.

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than  $\pm 2$  percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

**4.1 Fuel.** A 40 percent  $H_2$ /60 percent He or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

**4.2 Zero Gas.** High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon

\* Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

equivalent) or less than 0.1 percent of the span value, whichever is greater.

**4.3 Low-level Calibration Gas.** An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

**4.4 Mid-level Calibration Gas.** An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

**4.5 High-level Calibration Gas.** An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

#### 5. Measurement System Performance Specifications.

**5.1 Zero Drift.** Less than  $\pm 3$  percent of the span value.

**5.2 Calibration Drift.** Less than  $\pm 3$  percent of span value.

**5.3 Calibration Error.** Less than  $\pm 5$  percent of the calibration gas value.

#### 6. Pretest Preparations.

**6.1 Selection of Sampling Site.** The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters (whichever is less) upstream of the gas discharge to the atmosphere.

**6.2 Location of Sample Probe.** Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

**6.3 Measurement System Preparation.** Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics ( $> 1.0$  percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

**6.4 Calibration Error Test.** Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and

before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

**6.5 Response Time Test.** Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

#### 7. Emission Measurement Test

**7.1 Organic Measurement.** Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

**7.2 Drift Determination.** Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

#### 8. Organic Concentration Calculations.

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_m$$

Eq. 25A-1

Where:

$C_c$  = Organic concentration as carbon, ppmv.

$C_m$  = Organic concentration as measured, ppmv.

$K$  = Carbon equivalent correction factor.

$K = 2$  for ethane.

$K = 3$  for propane.

$K = 4$  for butane.

$K$  = Appropriate response factor for other organic calibration gases.

#### 9. Bibliography.

**9.1 Measurement of Volatile Organic Compounds—Guideline Series.** U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

**9.2 Traceability Protocol for Establishing True Concentrations of Gases Used for**

Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Research Triangle Park, N.C. June 1978.

**9.3 Gasoline Vapor Emission Laboratory Evaluation—Part 2.** U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, N.C. EMB Report No. 75-GAS-6. August 1975.

METHOD 25B DETERMINATION OF TOTAL GASEOUS ORGANIC  
CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes. (Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.) The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

2. Definitions

The terms and definitions are the same as for Method 25A.

3. Apparatus The apparatus are the same as for Method 25A with the exception of the following:

3.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

4. Calibration Gases

The calibration gases are the same as are required for Method 25A, Section 4. No fuel gas is required for an NDIR.

## 5. Measurement System Performance Specifications

5.1 Zero Drift. Less than  $\pm 3$  percent of the span value.

5.2 Calibration Drift. Less than  $\pm 3$  percent of the span value.

5.3 Calibration Error. Less than  $\pm 5$  percent of the calibration gas valve.

## 6. Pretest Preparations

6.1 Selection of Sampling Site. Same as in Method 25A, Section 6.1.

6.2 Location of Sample Probe. Same as in Method 25A, Section 6.2.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

6.4 Calibration Error Test. Same as in Method 25A, Section 6.4.

6.5 Response Time Test Procedure. Same as in Method 25A, Section 6.4.

## 7. Emission Measurement Test Procedure

Proceed with the emission measurement immediately upon satisfactory completion of the calibration.

7.1 Organic Measurement. Same as in Method 25A, Section 7.1.

7.2 Drift Determination. Same as in Method 25A, Section 7.2.

## 8. Organic Concentration Calculations

The calculations are the same as in Method 25A, Section 8.

## 9. Bibliography

The bibliography is the same as in Method 25A, Section 9.

**Method 25B—Determination of Total Gaseous Organic Concentration Using a Nondispersive Infrared Analyzer****1. Applicability and Principle.**

**1.1 Applicability.** This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes. (Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.) The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

**1.2 Principle.** A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

**2. Definitions.**

The terms and definitions are the same as for Method 25A.

**3. Apparatus.** The apparatus are the same as for Method 25A with the exception of the following:

**3.1 Organic Concentration Analyzer.** A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

**4. Calibration Gases.**

The calibration gases are the same as are required for Method 25A, Section 4. No fuel gas is required for an NDIR.

**5. Measurement System Performance Specifications.**

**5.1 Zero Drift.** Less than  $\pm 3$  percent of the span value.

**5.2 Calibration Drift.** Less than  $\pm 3$  percent of the span value.

**5.3 Calibration Error.** Less than  $\pm 5$  percent of the calibration gas value.

**6. Pretest Preparations.**

**6.1 Selection of Sampling Site.** Same as in Method 25A, Section 6.1.

**6.2 Location of Sampling Probe.** Same as in Method 25A, Section 6.2.

**6.3 Measurement System Preparation.** Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

**6.4 Calibration Error Test.** Same as in Method 25A, Section 6.4.

**6.5 Response Time Test Procedure.** Same as in Method 25A, Section 6.4.

**7. Emission Measurement Test Procedure.** Proceed with the emission measurement immediately upon satisfactory completion of the calibration.

**7.1 Organic Measurement.** Same as in Method 25A, Section 7.1.

**7.2 Drift Determination.** Same as in Method 25A, Section 7.2.

**8. Organic Concentration Calculations.** The calculations are the same as in Method 25A, Section 8.

**9. Bibliography.**

The bibliography is the same as in Method 25A, Section 9.

METHOD 27-DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE  
DELIVERY TANK USING PRESSURE-VACUUM TEST

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery tank which is equipped with vapor collection equipment.

1.2 Principle. Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

2. Definitions and Nomenclature

2.1 Gasoline. Any petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

2.2 Delivery tank. Any container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

2.3 Compartment. A liquid-tight division of a delivery tank.

2.4 Delivery tank vapor collection equipment. Any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

2.5 Time period of the pressure or vacuum test ( $t$ ). The time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

2.6 Initial pressure ( $P_i$ ). The pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm  $H_2O$ .



2.7 Initial vacuum ( $V_i$ ). The vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.8 Allowable pressure change ( $p$ ). The allowable amount of decrease in pressure during the static pressure test, within the time period  $t$ , as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.9 Allowable vacuum change ( $v$ ). The allowable amount of decrease in vacuum during the static vacuum test, within the time period  $t$ , as specified in the appropriate regulation, in mm H<sub>2</sub>O.

### 3. Apparatus

3.1 Pressure source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm H<sub>2</sub>O above atmospheric pressure.

3.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

3.3 Vacuum source. Vacuum pump capable of evacuating the delivery tank to 250 mm H<sub>2</sub>O below atmospheric pressure.

3.4 Pressure-vacuum supply hose.

3.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm H<sub>2</sub>O gauge pressure with  $\pm 2.5$  mm H<sub>2</sub>O precision.

3.6 Pressure-vacuum relief valves. The test apparatus shall be equipped with an in-line pressure-vacuum relief valve set to activate at 675 mm H<sub>2</sub>O above atmospheric pressure or 250 mm H<sub>2</sub>O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

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

3.8 Caps for liquid delivery hoses.

#### 4. Pretest Preparations

4.1 Summary. Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that, prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to attain completely these pretest conditions a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criterion in Sections 5.2.5 and 5.3.5.

4.2 Emptying of tank. The delivery tank shall be emptied of all liquid.

4.3 Purging of vapor. As much as possible, the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a much longer time for stabilization during the testing.

4.4 Temperature stabilization. As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

## 5. Test Procedure

### 5.1 Preparations.

#### 5.1.1 Open and close each dome cover.

#### 5.1.2 Connect static electrical ground connections to tank.

Attach the liquid delivery and vapor return hoses, remove the liquid delivery elbows, and plug the liquid delivery fittings. (Note: The purpose of testing the liquid delivery hoses is to detect tears or holes that would allow liquid leakage during a delivery. Liquid delivery hoses are not considered to be possible sources of vapor leakage, and thus, do not have to be attached for a vapor leakage test. Instead, a liquid delivery hose could be either visually inspected or filled with water to detect any liquid leakage.)

#### 5.1.3 Attach the test cap to the end of the vapor recovery hose.

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

5.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately as if it were an individual delivery tank.

### 5.2 Pressure test.

5.2.1 Connect the pressure source to the pressure-vacuum supply hose.

5.2.2 Open the shut-off valve in the vapor recovery hose cap. Applying air pressure slowly, pressurize the tank to  $P_i$ , the initial pressure specified in the regulation.

5.2.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of  $P_i$ . When the pressure stabilizes, record the time and initial pressure.

5.2.4 At the end of  $t$  minutes, record the time and final pressure.

5.2.5 Repeat steps 5.2.2 through 5.2.4 until the change in pressure for two consecutive runs agrees within  $\pm 12.5$  mm H<sub>2</sub>O. Calculate the arithmetic average of the two results.

5.2.6 Compare the average measured change in pressure to the allowable pressure change,  $\Delta p$ , as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

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

### 5.3 Vacuum test.

5.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

5.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to  $V_i$ , the initial vacuum specified in the regulation.

5.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of  $V_1$ . When the pressure stabilizes, record the time and initial vacuum.

5.3.4 At the end of  $t$  minutes, record the time and final vacuum.

5.3.5 Repeat steps 5.3.2 through 5.3.4 until the change in vacuum for two consecutive runs agrees within  $\pm 12.5$  mm  $H_2O$ . Calculate the arithmetic average of the two results.

5.3.6 Compare the average measured change in vacuum to the allowable vacuum change,  $\Delta v$ , as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

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

5.4 Post-test clean-up. Disconnect all test equipment and return the delivery tank to its pretest condition.

## 6. Alternative Procedures

6.1 The pumping of water into the bottom of a delivery tank is an acceptable alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

6.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

## Method 27—Determination of Vapor Tightness of Gasoline Delivery Tank Using Pressure-Vacuum Test

### 1. Applicability and Principle.

1.1 *Applicability.* This method is applicable for the determination of vapor tightness of a gasoline delivery tank which is equipped with vapor collection equipment.

1.2 *Principle.* Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

### 2. Definitions and Nomenclature.

2.1 *Gasoline.* Any petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

2.2 *Delivery tank.* Any container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

2.3 *Compartment.* A liquid-tight division of a delivery tank.

2.4 *Delivery tank vapor collection equipment.* Any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

2.5 *Time period of the pressure or vacuum test (t).* The time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

2.6 *Initial pressure (P<sub>i</sub>).* The pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.7 *Initial vacuum (V<sub>i</sub>).* The vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.8 *Allowable pressure change (Δp).* The allowable amount of decrease in pressure during the static pressure test, within the time period t, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.9 *Allowable vacuum change (Δv).* The allowable amount of decrease in vacuum during the static vacuum test, within the time period t, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

### 3. Apparatus.

3.1 *Pressure source.* Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm H<sub>2</sub>O above atmospheric pressure.

3.2 *Regulator.* Low pressure regulator for controlling pressurization of the delivery tank.

3.3 *Vacuum source.* Vacuum pump capable of evacuating the delivery tank to 250 mm H<sub>2</sub>O below atmospheric pressure.

3.4 *Pressure-vacuum supply hose.*

3.5 *Manometer.* Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm H<sub>2</sub>O gauge pressure with ±2.5 mm H<sub>2</sub>O precision.

3.6 *Pressure-vacuum relief valves.* The test apparatus shall be equipped with an in-line pressure-vacuum relief valve set to activate at 675 mm H<sub>2</sub>O above atmospheric pressure or 250 mm H<sub>2</sub>O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

3.7 *Test cap for vapor recovery hose.* This cap shall have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure-vacuum supply hose.

3.8 *Caps for liquid delivery hoses.*

### 4. Pretest Preparations.

4.1 *Summary.* Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that, prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to attain completely these pretest conditions a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criterion in Sections 5.2.5 and 5.3.5.

4.2 *Emptying of tank.* The delivery tank shall be emptied of all liquid.

4.3 *Purging of vapor.* As much as possible, the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a much longer time for stabilization during the testing.

4.4 *Temperature stabilization.* As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

### 5. Test Procedure.

#### 5.1 Preparations.

5.1.1 Open and close each dome cover.

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

(Note.—The purpose of testing the liquid delivery hoses is to detect tears or holes that would allow liquid leakage during a delivery. Liquid delivery hoses are not considered to be possible sources of vapor leakage, and thus, do not have to be attached for a vapor leakage test. Instead, a liquid delivery hose

could be either visually inspected, or filled with water to detect any liquid leakage.)

5.1.3 Attach the test cap to the end of the vapor recovery hose.

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

5.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately, as if it were an individual delivery tank.

#### 5.2 Pressure test.

5.2.1 Connect the pressure source to the pressure-vacuum supply hose.

5.2.2 Open the shut-off valve in the vapor recovery hose cap. Applying air pressure slowly, pressurize the tank to P<sub>i</sub>, the initial pressure specified in the regulation.

5.2.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of P<sub>i</sub>. When the pressure stabilizes, record the time and initial pressure.

5.2.4 At the end of t minutes, record the time and final pressure.

5.2.5 Repeat steps 5.2.2 through 5.2.4 until the change in pressure for two consecutive runs agrees within ±12.5 mm H<sub>2</sub>O. Calculate the arithmetic average of the two results.

5.2.6 Compare the average measured change in pressure to the allowable pressure change, Δp, as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

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

#### 5.3 Vacuum test.

5.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

5.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to V<sub>i</sub>, the initial vacuum specified in the regulation.

5.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of V<sub>i</sub>. When the pressure stabilizes, record the time and initial vacuum.

5.3.4 At the end of t minutes, record the time and final vacuum.

5.3.5 Repeat steps 5.3.2 through 5.3.4 until the change in vacuum for two consecutive runs agrees within ±12.5 mm H<sub>2</sub>O. Calculate the arithmetic average of the two results.

5.3.6 Compare the average measured change in vacuum to the allowable vacuum change, Δv, as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

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

5.4 *Post-test clean-up.* Disconnect all test equipment and return the delivery tank to its pretest condition.

### 6. Alternative Procedures.

6.1 The pumping of water into the bottom of a delivery tank is an acceptable

alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

6.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

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**BILLING CODE 6000-60-M**



METHOD 106--DETERMINATION OF VINYL CHLORIDE  
FROM STATIONARY SOURCES

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle

1.1 Applicability. The method is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. The method does not measure vinyl chloride contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to GC analysis using a flame ionization detector (FID).

2. Range and Sensitivity

This method is designed for the 0.1 to 50 ppm range. However, common GC instruments are capable of detecting 0.02 ppm vinyl chloride. With proper calibration, the upper limit may be extended as needed.

### 3. Interferences

The chromatographic columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

### 4. Apparatus

4.1 Sampling (see Figure 106-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing (as stack temperature permits) equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 106-1.

4.1.4 Tedlar Bags. 50- to 100-liter capacity, to contain sample. Aluminized Mylar bags may be used if the samples are analyzed within 24 hours of collection.

4.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rates.

4.1.7 Pump. Leak-free, with minimum of 2-liter/min capacity.

4.1.8 Charcoal Tube. To prevent admission of vinyl chloride and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flowmeter. For observing sampling flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

4.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 106-1).

4.1.11 Tubing Fittings and Connectors. Teflon or stainless steel, to assemble sampling train.

4.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to GC sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon conclusion of analysis of those bags.

4.3 Analysis. The following equipment is required:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0- to 5.0-ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppm vinyl chloride that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the wave form, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.")

4.3.2.1 Column A. Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102.

4.3.2.2 Column B. Stainless steel, 2.0 m by 3.2 mm, containing 20 percent GE SF-96 on 60/80-mesh Chromasorb P AW; or stainless steel, 1.0 m by 3.2 mm containing 80/100-mesh Porapak T. Column B is required as a secondary column if acetaldehyde is present. If used, column B is placed after column A. The combined columns should be operated at 120° C.

4.3.3 Flowmeters (2). Rotameter type, 100-ml/min capacity, with flow control valves.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to 1° C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around GC during sample analysis.

4.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

4.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator on recorder, to measure chromatograph peak areas.

4.4 Calibration. Sections 4.4.2 through 4.4.4 are for the optional procedure in Section 7.1.

4.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar Bags. Sixteen-inch-square size, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringes. 0.5-ml and 50- $\mu$ l, gas tight, individually calibrated to dispense gaseous vinyl chloride.

4.4.4 Dry Gas Meter, with Temperature and Pressure Gauges. Singer model DTM-115 with 802 index, or equivalent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

## 5. Reagents

Use only reagents that are of chromatograph grade.

5.1 Analysis. The following are required for analysis.

5.1.1 Helium or Nitrogen. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen. Zero grade.

5.1.3 Oxygen or Air. Zero grade, as required by the detector.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl Chloride. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride, for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50-, 10-, and 5-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating

his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 50 and 100 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

#### 5.2.3.2 Verification of Manufacturer's Calibration Standards.

Before using a standard, the manufacturer shall verify each calibration standard (a) by comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 or (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (vinyl chloride in nitrogen cylinders). The concentrations of the audit cylinders should be: one low-concentration cylinder in the range of 5 to 20 ppm vinyl chloride and one high-concentration cylinder in the range of 20 to 50 ppm. 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 cylinders as described in Section 5.2.3.1, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined here to mean analysis performed by an individual different 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  $\pm 5$  percent of the gas manufacturer's concentration.



## 6. Procedure

6.1 Sampling. Assemble the sample train as shown in Figure 106-1. A bag leak check should have been performed previously according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. 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 that will fill over 50 percent of bag volume in the specified sample period. After allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. At all times, 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. Protect the bag container from sunlight.

6.2 Sample storage. Keep the sample bags out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection. Aluminized Mylar bag samples must be analyzed within 24 hours.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas

passes from the sample valve to 100-ml/min rotameter with flow control valve followed by a charcoal tube and a 1-in.  $H_2O$  pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to  $100^{\circ}C$  and the detector temperature to  $150^{\circ}C$ . When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatography operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for 30 seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the  $H_2O$  manometer, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), sample number, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to vinyl chloride as determined in Section 7.2.1. Measure the vinyl chloride peak area,  $A_m$ , by use of a disc integrator, electronic

integrator, or a planimeter. Measure and record the peak heights,  $H_m$ . Record  $A_m$  and retention time. Repeat the injection at least two times or until two consecutive values for the total area of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

Compare the ratio of  $H_m$  to  $A_m$  for the vinyl chloride sample with the same ratio for the standard peak that is closest in height. If these ratios differ by more than 10 percent, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2.2).

6.5 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.)

## 7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance

### 7.1 Preparation of Vinyl Chloride Standard Gas Mixtures.

(Optional Procedure--delete if cylinder standards are used.) Evacuate a 16-inch square Tedlar bag that has passed a leak check (described in Section 7.3.2) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5-ml syringe to inject 250  $\mu$ l of 99.9+ percent vinyl chloride gas through the wall of the bag. Upon withdrawing the

syringe, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the 50  $\mu$ l syringe to prepare gas mixtures having 10- and 5-ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time new gas mixtures must be prepared. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

## 7.2 Calibration.

7.2.1 Determination of Vinyl Chloride Retention Time. (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4 above. Determine proper attenuator 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 vinyl chloride. Maintain conditions with the equipment plumbing arranged identically to Section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs.

This quantity divided by the chart speed is defined as the retention time. Since other organics may be present in the sample, positive identification of the vinyl chloride peak must be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a GC measurement of each gas mixture standard (described in Section 5.2.3 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard mixtures, and activate the sample valve. Record the concentration of vinyl chloride injected ( $C_c$ ), attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent. For each group of sample analyses, use the average of the two calibration curves which bracket that group 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.

### 7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. Checking of bags for leaks is required after bag use and strongly recommended before bag use. After each use, connect a water manometer and pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O and allow it to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

## 8. Calculations

8.1 Determine the sample peak area,  $A_c$ , as follows:

$$A_c = A_m A_f \quad \text{Eq. 106-1}$$

Where:

$A_m$  = Measured peak area.

$A_f$  = Attenuation factor.

8.2 Vinyl Chloride Concentrations. From the calibration curves described in Section 7.2.2, determine the average concentration value of vinyl chloride,  $C_c$ , that corresponds to  $A_c$ , the sample peak area. Calculate the concentration of vinyl chloride in the bag,  $C_b$ , as follows:

$$C_b = \frac{C_c P_r T_i}{P_i T_r (1 - B_{wb})} \quad \text{Eq. 106-2}$$

Where:

$P_r$  = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

$T_i$  = Sample loop temperature on the absolute scale at the time of analysis, °K.

$P_i$  = Laboratory pressure at time of analysis, mm Hg.

$T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K.

$B_{wb}$  = Water vapor content of the bag sample, as analyzed.

## 9. Bibliography

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3. Midwest Research Institute. Standardization of Stationary Source Emission Method for Vinyl Chloride. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-026. May 1977.
4. Scheil, G. and M.C. Sharp. Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/4-78-058. October 1978.



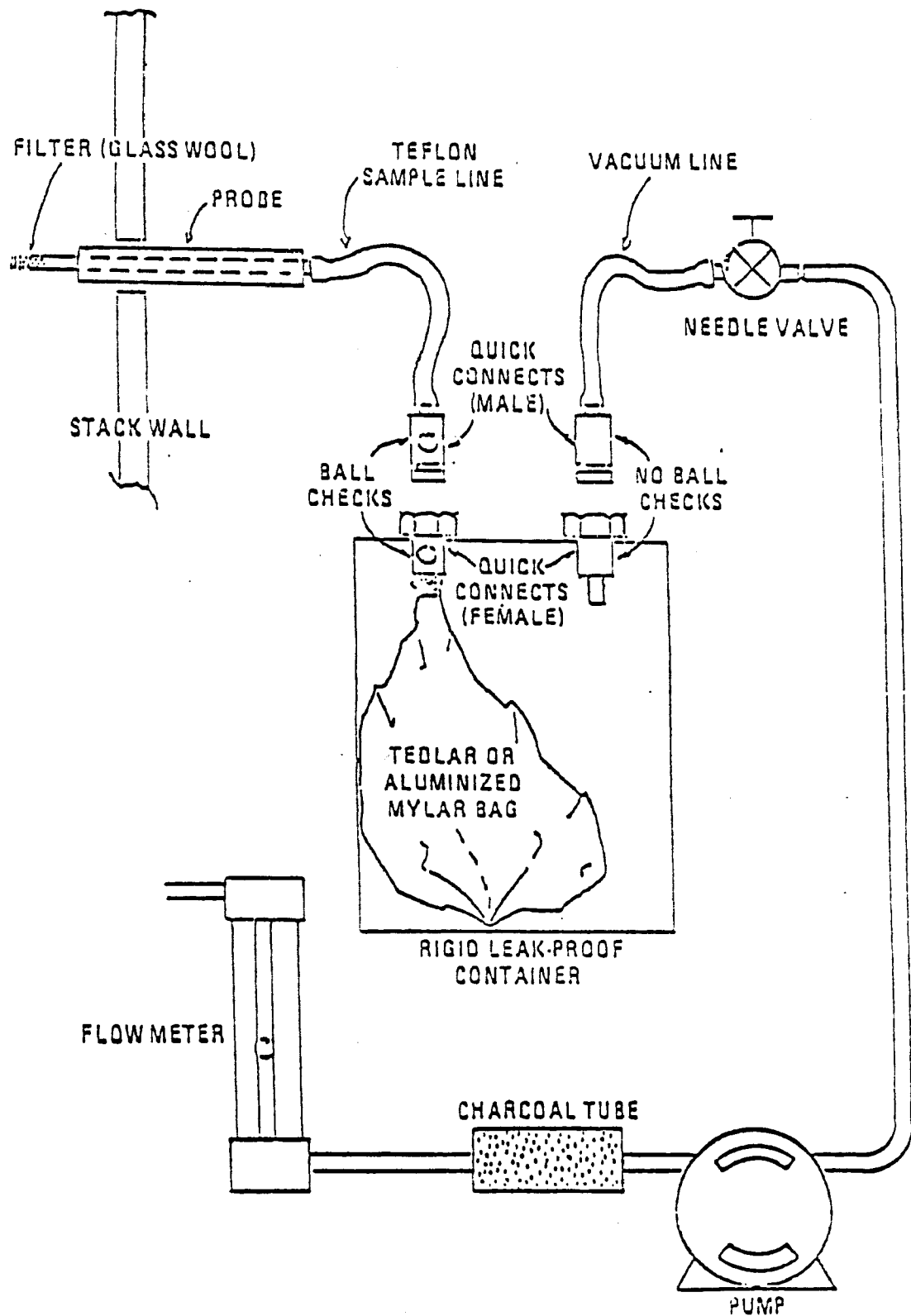


Figure 106-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. The method does not measure vinyl chloride contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to GC analysis using a flame ionization detector (FID).

## 2. Range and Sensitivity

This method is designed for the 0.1 to 50 ppm range. However, common GC instruments are capable of detecting 0.02 ppm vinyl chloride. With proper calibration, the upper limit may be extended as needed.

## 3. Interferences

The chromatographic columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic, provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

## 4. Apparatus

4.1 Sampling (see Figure 106-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing (as stack temperature permits) equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon completion of the test.

4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 106-1.

4.1.4 Tedlar Bags. 50- to 100-liter capacity, to contain sample. Aluminized Mylar bags may be used if the samples are analyzed within 24 hours of collection.

4.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rates.

4.1.7 Pump. Leak-free, with minimum of 2-liter/min capacity.

4.1.8 Charcoal Tube. To prevent admission of vinyl chloride and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flowmeter. For observing sampling flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

4.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 106-1).

4.1.11 Tubing Fittings and Connectors. Teflon or stainless steel, to assemble sampling train.

4.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to GC sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test, and discard upon conclusion of analysis of those bags.

4.3 Analysis. The following equipment is required:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0- to 5.0-ml heated sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppm vinyl chloride that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the wave form, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.")

4.3.2.1 Column A. Stainless steel, 2.0 m by 3.2 mm, containing 80/100-mesh Chromasorb 102.

4.3.2.2 Column B. Stainless steel, 2.0 m by 3.2 mm, containing 20 percent GE SF-96 on 60/80-mesh Chromasorb P AW; or stainless steel, 1.0 m by 3.2 mm containing 80/100-mesh Porapak T. Column B is required as a secondary column if acetaldehyde is present. If used, column B is placed after column A. The combined columns should be operated at 120° C.

4.3.3 Flowmeters (2). Rotameter type, 100-ml/min capacity, with flow control valves.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to 1° C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around GC during sample analysis.

4.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

4.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator on recorder, to measure chromatograph peak areas.

4.4 Calibration. Sections 4.4.2 through 4.4.4 are for the optional procedure in Section 7.1.

4.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar Bags. Sixteen-inch-square size, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringes. 0.5-ml and 50-μl, gas tight, individually calibrated to dispense gaseous vinyl chloride.

## Method 106—Determination of Vinyl Chloride From Stationary Sources

### Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

### 1. Applicability and Principle

1.1 Applicability. The method is applicable to the measurement of vinyl chloride in stack gases from ethylene

4.4.4 Dry Gas Meter, with Temperature and Pressure Gauges. Singer model DTM-115 with 802 index, or equivalent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

#### 5. Reagents

Use only reagents that are of chromatograph grade.

5.1 Analysis. The following are required for analysis.

5.1.1 Helium or Nitrogen. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen. Zero grade.

5.1.3 Oxygen or Air. Zero grade, as required by the detector.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Vinyl Chloride. Pure vinyl chloride gas certified by the manufacturer to contain a minimum of 99.9 percent vinyl chloride, for use in the preparation of standard gas mixtures in Section 7.1. If the gas manufacturer maintains a bulk cylinder supply of 99.9+ percent vinyl chloride, the certification analysis may have been performed on this supply rather than on each gas cylinder prepared from this bulk supply. The date of gas cylinder preparation and the certified analysis must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.2.2 Nitrogen. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50-, 10-, and 5-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 50 and 100 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source

of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards. Before using a standard, the manufacturer shall verify each calibration standard (a) by comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 or (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (vinyl chloride in nitrogen cylinders). The concentrations of the audit cylinder should be: one low-concentration cylinder in the range of 5 to 20 ppm vinyl chloride and one high-concentration cylinder in the range of 20 to 50 ppm. 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, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined here to mean analysis performed by an individual different 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  $\pm 5$  percent of the gas manufacturer's concentration.

#### 6. Procedure

6.1 Sampling. Assemble the sample train as shown in Figure 106-1. A bag leak check should have been performed previously according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connection between the bag and the probe are tight. 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 that will fill over 50 percent of bag volume in the specific sample period. After allowing sufficient time to purge the line several times, change the vacuum line from the container to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate proportional to the stack velocity. At all times, 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. Protect the bag container from sunlight.

6.2 Sample storage. Keep the sample bags out of direct sunlight. When at all possible, analysis is to be performed within 24 hours, but in no case in excess of 72 hours of sample collection. Aluminized Mylar bag samples must be analyzed within 24 hours.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to 100-ml/min-rotameter with flow control valve followed by a charcoal tube and a 1-in.  $H_2O$  pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to 100° C and the detector temperature to 150° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatography operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 40 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for 30-seconds at the rate of 100 ml/min, shut off flow, allow the sample loop pressure to reach atmospheric pressure as indicated by the  $H_2O$  manometer, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), sample number, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to vinyl chloride as determined in Section 7.2.1. Measure the vinyl chloride peak area,  $A_m$ , by use of a disc integrator, electronic integrator, or a planimeter. Measure and record the peak heights,  $H_m$ . Record  $A_m$  and retention time. Repeat the injection at least two times or until two consecutive values for the total area of the vinyl chloride peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

Compare the ratio of  $H_m$  to  $A_m$  for the vinyl chloride sample with the same ratio for the standard peak that is closest in height. If these ratios differ by more than 10 percent, the vinyl chloride peak may not be pure (possibly acetaldehyde is present) and the secondary column should be employed (see Section 4.3.2.2).

6.5 Determination of Bag Water Vapor Content. Measure the ambient temperature

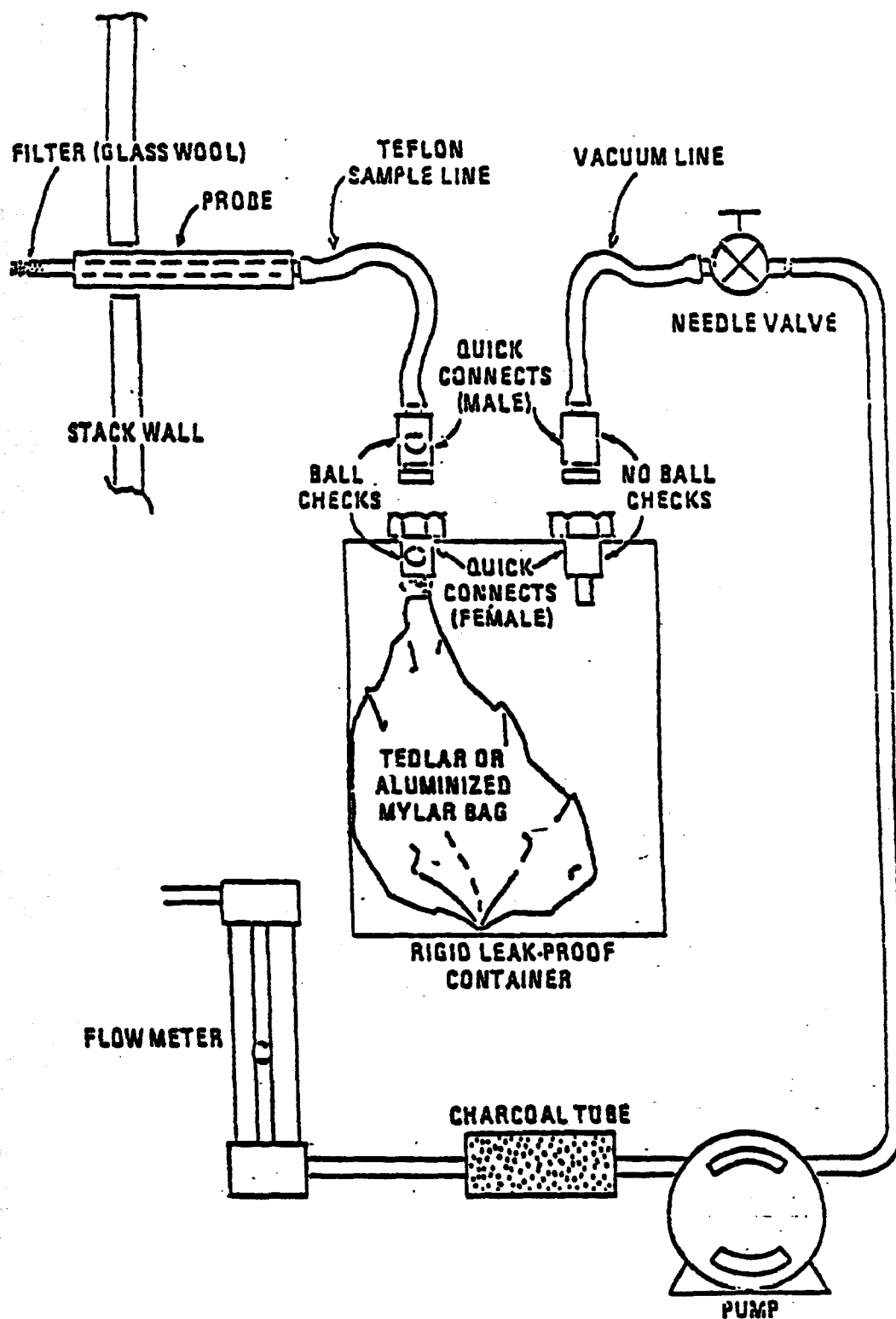


Figure 106-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

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.)

#### 7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance

**7.1 Preparation of Vinyl Chloride Standard Gas Mixtures.** (Optional Procedure—delete if cylinder standards are used.) Evacuate a 16-inch square Tedlar bag that has passed a leak check (described in Section 7.3.2) and meter in 5.0 liters of nitrogen. While the bag is filling, use the 0.5-ml syringe to inject 250  $\mu$ l of 99.9+ percent vinyl chloride gas through the wall of the bag. Upon withdrawing the syringe, immediately cover the resulting hole with a piece of adhesive tape. The bag now contains a vinyl chloride concentration of 50 ppm. In a like manner use the 50  $\mu$ l syringe to prepare gas mixtures having 10- and 5-ppm vinyl chloride concentrations. Place each bag on a smooth surface and alternately depress opposite sides of the bag 50 times to further mix the gases. These gas mixture standards may be used for 10 days from the date of preparation, after which time new gas mixtures must be prepared. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

#### 7.2 Calibration.

**7.2.1 Determination of Vinyl Chloride Retention Time.** (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4 above. Determine proper attenuator 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 vinyl chloride. Maintain conditions with the equipment plumbing arranged identically to Section 6.3, and flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the vinyl chloride calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to vinyl chloride. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity divided by the chart speed is defined as the retention time. Since other organics may be present in the sample, positive identification of the vinyl chloride peak must be made.

**7.2.2 Preparation of Chromatograph Calibration Curve.** Make a GC measurement

of each gas mixture standard (described in Section 5.2.3 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard mixtures, and activate the sample valve. Record the concentration of vinyl chloride injected ( $C_c$ ), attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after the analysis of each emission test set of bag samples, whichever is more frequent. For each group of sample analyses, use the average of the two calibration curves which bracket that group 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.

#### 7.3 Quality Assurance.

**7.3.1 Analysis Audit.** Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis."

**7.3.2 Bag Leak Checks.** Checking of bags for leaks is required after bag use and strongly recommended before bag use. After each use, connect a water manometer and pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O and allow it to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

#### 8. Calculations.

**8.1 Determine the sample peak area,  $A_m$ , as follows:**

$$A_c = A_m A_f \quad \text{Eq. 106-1}$$

Where:

$A_m$  = Measured peak area.

$A_f$  = Attenuation factor.

**8.2 Vinyl Chloride Concentrations.** From the calibration curves described in Section 7.2.2, determine the average concentration value of vinyl chloride,  $C_b$ , that corresponds to  $A_c$ , the sample peak area. Calculate the concentration of vinyl chloride in the bag,  $C_p$ , as follows:

$$C_b = \frac{C_c P_r T_1}{P_1 T_r (1 - B_{wb})} \quad \text{Eq. 106-2}$$

Where:

$P_r$  = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

$T_1$  = Sample loop temperature on the absolute scale at the time of analysis, °K.

$P_1$  = Laboratory pressure at time of analysis, mm Hg.

$T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K.

$B_{wb}$  = Water vapor content of the bag sample, as analyzed.

#### 9. Bibliography.

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3. Midwest Research Institute. Standardization of Stationary Source Emission Method for Vinyl Chloride. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-77-026. May 1977.

4. Scheil, G. and M.C. Sharp. Collaborative Testing of EPA Method 106 (Vinyl Chloride) that Will Provide for a Standardized Stationary Source Emission Measurement Method. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/4-78-058. October 1978.

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METHOD 107--DETERMINATION OF VINYL CHLORIDE CONTENT OF INPROCESS  
WASTEWATER SAMPLES, AND VINYL CHLORIDE CONTENT OF POLYVINYL CHLORIDE  
RESIN, SLURRY, WET CAKE, AND LATEX SAMPLES

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC), nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of the vinyl chloride monomer (VCM) content of inprocess wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq. (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

1.2 Principle. The basis for this method relates to the vapor equilibrium that is established between RVCM, PVC resin, water, and air in a closed system. The RVCM in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

## 2. Range and Sensitivity

The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include  $1 \times 10^{-7}$  mg and  $4 \times 10^{-7}$  mg. With proper calibration, the upper limit may be extended as needed.

## 3. Interferences

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

## 4. Precision and Reproducibility

An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 5.29 percent for a sample with a mean of 62.66 ppm.

## 5. Safety

Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air

mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

## 6. Apparatus

6.1 Sampling. The following equipment is required:

6.1.1 Glass Bottles. 60-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

6.1.2 Glass Vials. 50-ml capacity Hypo-vial, sealed with Teflon faced Tuf-Bond discs, for water samples.

6.1.3 Adhesive Tape. To prevent loosening of bottle tops.

6.2 Sample Recovery. The following equipment is required:

6.2.1 Glass Vials. With butyl rubber septa, Perkin-Elmer Corporation Nos. 0105-0129 (glass vials), B001-0728 (gray butyl rubber septum, plug style), 0105-0131 (butyl rubber septa), or equivalents. The seals must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.2.2 Analytical Balance. Capable of weighing to  $\pm 0.0001$  gram.

6.2.3 Vial Sealer. Perkin-Elmer No. 105-0106, or equivalent.

6.2.4 Syringe. 100- $\mu$ l capacity, precision series "A" No. 010025, or equivalent.

6.3 Analysis. The following equipment is required:



6.3.1 Gas Chromatograph. Perkin-Elmer Corporation Model F-40, F-42, or F-45 Head-Space Analyzer, or equivalent. Equipped with backflush accessory.

6.3.2 Chromatographic Columns. Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbopak B, have been suggested for samples containing acetaldehyde.

6.3.3 Thermometer. 0 to 100° C, accurate to  $\pm 0.1^\circ$  C, Perkin-Elmer No. 105-0109, or equivalent.

6.3.4 Sample Tray Thermostat System. Perkin-Elmer No. 105-0103, or equivalent.

6.3.5 Septa. Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105-1008, or equivalent.

6.3.6 Integrator-Recorder. Hewlett-Packard Model 3380A, or equivalent.

6.3.7 Filter Drier Assembly (3). Perkin-Elmer No. 2230117, or equivalent.

6.3.8 Soap Film Flowmeter. Hewlett Packard No. 0101-0113, or equivalent.

6.3.9 Regulators. For required gas cylinders.

6.3.10 Headspace Vial Pre-Pressurizer. Nitrogen pressurized hypodermic needle inside protective shield. (Blueprint available from Test Support Section, Emission Measurement Branch, Office of Air Quality Planning and Standards, Environmental Protection Agency, Mail Drop 19, Research Triangle Park, N.C. 27711.)

## 7. Reagents

Use only reagents that are of chromatographic grade.

7.1 Analysis. The following items are required for analysis:

7.1.1 Hydrogen. Zero grade.

7.1.2 Nitrogen. Zero grade.

7.1.3 Air. Zero grade.

7.2 Calibration. The following items are required for calibration:

7.2.1 Cylinder Standards (4). Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 9.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl

chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 8000 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the

verification concentration value must be within +5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

## 8. Procedure

### 8.1 Sampling.

8.1.1 PVC Sampling. Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

8.1.2 Water Sampling. Prior to use, the 50-ml vials (without the discs) must be capped with aluminum foil and heated in a muffle furnace at 400° C for at least 1 hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, with the Teflon side down, on the opening of the vial.

Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

8.2 Sample Recovery. Samples must be run within 24 hours.

8.2.1 Resin Samples. The weight of the resin used must be between 3.5 and 4.5 grams. An exact weight must be obtained ( $\pm 0.0001$  g) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100  $\mu$ l or about two equal drops of distilled water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVCM. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90° C bath. Do not exceed 5 hours.

Note: Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

8.2.2 Suspension Resin Slurry and Wet Cake Samples. Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place

approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight ( $\pm 0.0001$  g). All samples must be prepressurized and then conditioned for 1 hour at 90° C. A sample of wet cake is used to determine total solids (TS). This is required for calculating the RVCm.

8.2.3 Dispersion Resin Slurry and Geon Latex Samples. The materials should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight ( $\pm 0.0001$  g). After prepressurization, condition the vial for 1 hour at 90° C in the analyzer bath. Determine the TS on the slurry sample (Section 8.3.5).

8.2.4 Inprocess Wastewater Samples. Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight ( $\pm 0.0001$  g). Prepressurize the vial, and then condition for 1 to 2 hours as required at 90° C in the analyzer bath.

### 8.3 Analysis

8.3.1 Preparation of Equipment. Install the chromatographic column and condition overnight at 160° C. In the first operation, Porapak columns must be purged for 1 hour at 230° C.

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

8.3.1.1 Flow Rate Adjustments. Adjust flow rates as follows:

a. Nitrogen Carrier Gas. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to produce a flow rate of 30.0 cc/min. Accurately measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

b. Vial Prepressurizer Nitrogen. After the nitrogen carrier is set, solve the following equation and adjust the pressure on the vial prepressurizer accordingly.

$$P = \frac{T_1}{T_2} \left[ P_1 - \frac{P_{w1} - P_{w2}}{7.50} \right] - 10 \text{ k Pa}$$

Where:

$T_1$  = Ambient temperature, °K.

$T_2$  = Conditioning bath temperature, °K.

$P_1$  = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.

$P_{w1}$  = Water vapor pressure @ 90° C (525.8 mm Hg).

$P_{w2}$  = Water vapor pressure @ 22° C (19.8 mm Hg).

7.50 = mm Hg per k Pa.

10 k Pa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated pressure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90° C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.

c. Burner Air Supply. Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/min. Check with bubble flowmeter.

d. Hydrogen Supply. Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately  $35 \pm 5$  cc/min. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

8.3.1.2 Temperature Adjustments. Set temperatures as follows:

- a. Oven (chromatograph column), 140° C.
- b. Dosing Line, 150° C.
- c. Injection Block, 170° C.
- d. Sample Chamber, Water Temperature, 90° C  $\pm$  1.0° C.



8.3.1.3 Ignition of Flame Ionization Detector. Ignite the detector according to the manufacturer's instructions.

8.3.1.4 Amplifier Balance. Balance the amplifier according to the manufacturer's instructions.

8.3.2 Programming the Chromatograph. Program the chromatograph as follows:

- a. I-Dosing or Injection Time. The normal setting is 2 seconds.
- b. A-"Analysis Time." The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.
- c. B-Backflushing Time. The normal setting is double the "analysis time."
- d. W-Stabilization Time. The normal setting is 0.5 min to 1.0 min.
- e. X-Number of Analyses Per Sample. The normal setting is one.

8.3.3 Preparation of Sample Turntable. Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. All samples and standards must be pressurized for 60 seconds by using the vial prepressurizer. The numbered sample vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Positions 1 and 2--Old 2000-ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3 -- 50-ppm standard, freshly prepared.

Position 4 -- 500-ppm standard, freshly prepared.

Position 5 -- 2000-ppm standard, freshly prepared.

Position 6 -- 4000-ppm standard, freshly prepared.

Position 7 -- Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50-, 500-, 2000-, and 4000-ppm standards. Samples, including standards, must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

8.3.4 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

8.3.5 Determination of TS. For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing, return the pan to the oven for a short period of time, and then reweigh to verify complete dryness. The TS are then calculated as the final sample weight divided by initial sample weight.

## 9. Calibration

Calibration is to be performed each 8-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two 2000-ppm standards from the previous day.

9.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100  $\mu$ l or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a 1/8-in. stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to fill the vials. After purging, reduce the flow rate to 500 to 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the 1/8-in. filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole.

## 9.2 Preparation of Chromatograph Calibration Curve.

Prepare two 50-, 500-, 2000-, and 4000-ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot  $A_s$ , the integrator area counts for each standard sample, versus  $C_c$ , the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

## 10. Calculations

10.1 Response Factor. If the calibration curve described in Section 9.2 passes through zero, a response factor,  $R_f$ , may be used to compute vinyl chloride concentrations. To compute a response factor, divide any particular  $A_s$  by the corresponding  $C_c$ .

$$R_f = \frac{A_s}{C_c} \quad \text{Eq. 107-1}$$

If the calibration curve does not pass through zero, the calibration curve must be employed to calculate each sample concentration unless the error introduced by using a particular  $R_f$  is known.

10.2 Residual Vinyl Chloride Monomer Concentration, ( $C_{rvc}$ ) or Vinyl Chloride Monomer Concentration. Calculate  $C_{rvc}$  in ppm or mg/kg as follows:

$$C_{rvc} = \frac{A_s P_a}{R_f T_1} \left[ \frac{M_v V_g}{R m} + K_p (TS) T_2 + K_w (1 - TS) T_2 \right] \quad \text{Eq. 107-2}$$

Where:

$A_s$  = Chromatograph area counts of vinyl chloride for the sample.

$P_a$  = Ambient atmospheric pressure, mm Hg.

$R_f$  = Response factor in area counts per ppm VCM.

$T_1$  = Ambient laboratory temperature, °K.

$M_v$  = Molecular weight of VCM, 62.5 g/mole.

$V_g$  = Volume of the vapor phase,  $\text{cm}^3$ .

$R$  = Gas constant, ( $62360 \text{ cm}^3$ ) (mm Hg/mole) (°K).

$m$  = Sample weight, g.

$K_p$  = Henry's Law Constant for VCM in PVC @ 90° C,  
 $6.52 \times 10^{-6}$  g/g/mm Hg.

TS = Total solids expressed as a decimal fraction.

$T_2$  = Equilibrium temperature, °K.

$K_w$  = Henry's Law Constant for VCM in water @ 90° C,  
 $7 \times 10^{-7}$  g/g/mm Hg.

Assuming the following conditions are met, these values can be substituted into Equation 107-2:

$P_a$  = 750 mm Hg.

$V_g$  = Vial volume - sample volume (Fisher vials are 22.0 cm<sup>3</sup> and Perkin-Elmer vials are 21.8 cm<sup>3</sup>).

$T_1$  = 23° C or 296° K.

$T_2$  = 90° C or 363° K.

$$rvc = \frac{A_s}{R_f} \frac{750}{296} \left[ \frac{65.5 \left( 21.8 - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653} \right)}{62360 m} + 6.25 \times 10^{-6} (TS)(363) + 7.0 \times 10^{-7} (1-TS)(363) \right]$$

Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

## 11. References

1. B.F. Goodrich. Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio. October 8, 1979.

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5. Mansfield, R.A. The Evaluation of Henry's Law Constant (Kp) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich. Avon Lake, Ohio. February 10, 1978.

**Method 187—Determination of Vinyl Chloride Content of Inprocess Wastewater Samples, and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, Wet Cake, and Latex Samples**

**Introduction**

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC), nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

**1. Applicability and Principle.**

**1.1 Applicability.** This method applies to the measurement of the vinyl chloride monomer (VCM) content of inprocess wastewater samples, and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, slurry, and latex samples. It cannot be used for polymer in fused forms, such as sheet or cubes. This method is not acceptable where methods from Section 304(h) of the Clean Water Act, 33 U.S.C. 1251 et seq. (the Federal Water Pollution Control Amendments of 1972 as amended by the Clean Water Act of 1977) are required.

**1.2 Principle.** The basis for this method relates to the vapor equilibrium that is established between RVCM, PVC resin, water, and air in a closed system. The RVCM in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

**2. Range and Sensitivity.** The lower limit of detection of vinyl chloride will vary according to the chromatograph used. Values reported include  $1 \times 10^{-7}$  mg and  $4 \times 10^{-7}$  mg. With proper calibration, the upper limit may be extended as needed.

**3. Interferences.** The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

**4. Precision and Reproducibility.** An interlaboratory comparison between seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.83 percent for a sample with a mean of 2.09 ppm, 4.18 percent for a sample with a mean of 1.86 ppm, and 5.29 percent for a sample with a mean of 62.86 ppm.

**5. Safety.** Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be

routed to outside air. Vinyl chloride, even at low ppm levels, must never be vented inside the laboratory. After vials have been analyzed, the gas must be vented prior to removal of the vial from the instrument turntable. Vials must be vented through a hypodermic needle connected to an activated charcoal tube to prevent release of vinyl chloride into the laboratory atmosphere. The charcoal must be replaced prior to vinyl chloride breakthrough.

**6. Apparatus.**

**6.1 Sampling.** The following equipment is required:

**6.1.1 Glass bottles.** 80-ml (2-oz) capacity, with wax-lined screw-on tops, for PVC samples.

**6.1.2 Glass Vials.** 50-ml capacity Hypo-vial, sealed with Teflon faced Tuf-Bond discs, for water samples.

**6.1.3 Adhesive Tape.** To prevent loosening of bottle tops.

**6.2 Sample Recovery.** The following equipment is required:

**6.2.1 Glass Vials.** With butyl rubber septa, Perkin-Elmer Corporation Nos. 0105-0129 (glass vials), B001-0728 (gray butyl rubber septum, plug style), 0105-0131 (butyl rubber septa), or equivalents. The seals must be made from butyl rubber. Silicone rubber seals are not acceptable.

**6.2.2 Analytical Balance.** Capable of weighing to  $\pm 0.0001$  gram.

**6.2.3 Vial Sealer.** Perkin-Elmer No. 105-0106, or equivalent.

**6.2.4 Syringe.** 100- $\mu$ l capacity, precision series "A" No. 010025, or equivalent.

**6.3 Analysis.** The following equipment is required:

**6.3.1 Gas Chromatograph.** Perkin-Elmer Corporation Model F-40, F-42, or F-45 Headspace Analyzer, or equivalent. Equipped with backflush accessory.

**6.3.2 Chromatographic Columns.** Stainless steel 1 m by 3.2 mm and 2 m by 3.2 mm, both containing 50/80-mesh Porapak Q. The analyst may use other columns provided that the precision and accuracy of the analysis of vinyl chloride standards are not impaired and he has available for review information confirming that there is adequate resolution of the vinyl chloride peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution.") Two 1.83 m columns, each containing 1 percent Carbowax 1500 on Carbowax B, have been suggested for samples containing acetaldehyde.

**6.3.3 Thermometer.** 0 to 100° C, accurate to  $\pm 0.1^\circ$  C, Perkin-Elmer No. 105-0108, or equivalent.

**6.3.4 Sample Tray Thermostat System.** Perkin-Elmer No. 105-0103, or equivalent.

**6.3.5 Septa.** Sandwich type, for automatic dosing, 13 mm, Perkin-Elmer No. 105-1008, or equivalent.

**6.3.6 Integrator-Recorder.** Hewlett-Packard Model 3380A, or equivalent.

**6.3.7 Filter Drier Assembly (3).** Perkin-Elmer No. 2230117, or equivalent.

**6.3.8 Soap Film Flowmeter.** Hewlett-Packard No. 0101-0113, or equivalent.

**6.3.9 Regulators.** For required gas cylinders.

**6.3.10 Headspace Vial Pre-Pressurizer.** Nitrogen pressurized hypodermic needle inside protective shield. (Blueprint available from Test Support Section, Emission Measurement Branch, Office of Air Quality Planning and Standards, Environmental Protection Agency, Mail Drop 19, Research Triangle Park, N.C. 27711.)

**7. Reagents.** Use only reagents that are of chromatographic grade.

**7.1 Analysis.** The following items are required for analysis:

**7.1.1 Hydrogen.** Zero grade.

**7.1.2 Nitrogen.** Zero grade.

**7.1.3 Air.** Zero grade.

**7.2 Calibration.** The following items are required for calibration:

**7.2.1 Cylinder Standards (4).** Gas mixture standards (50-, 500-, 2000- and 4000-ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 9.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 7.2.1.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

**7.2.1.1 Cylinder Standards Certification.** The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 4000 and 8000 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

**7.2.1.2 Verification of Manufacturer's Calibration Standards.** Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards, if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$

percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

#### 8. Procedure.

##### 8.1 Sampling.

**8.1.1 PVC Sampling.** Allow the resin or slurry to flow from a tap on the tank or silo until the tap line has been well purged. Extend and fill a 60-ml sample bottle under the tap, and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

**8.1.2 Water Sampling.** Prior to use, the 50-ml vials (without the discs) must be capped with aluminum foil and heated in a muffle furnace at 400° C for at least 1 hour to destroy or remove any organic matter that could interfere with analysis. At the sampling location fill the vials bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, with the Teflon side down, on the opening of the vial. Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed.

**8.2 Sample Recovery.** Samples must be run within 24 hours.

**8.2.1 Resin Samples.** The weight of the resin used must be between 3.5 and 4.5 grams. An exact weight must be obtained ( $\pm 0.0001$  g) for each sample. In the case of suspension resins, a volumetric cup can be prepared for holding the required amount of sample. When the cup is used, open the sample bottle, and add the cup volume of resin to the tared sample vial (tared, including septum and aluminum cap). Obtain the exact sample weight, add 100  $\mu$ l or about two equal drops of distilled water, and immediately seal the vial. Report this value on the data sheet; it is required for calculation of RVC. In the case of dispersion resins, the cup cannot be used. Weigh the sample in an aluminum dish, transfer the sample to the tared vial, and accurately weigh it in the vial. After prepressurization of the samples, condition them for a minimum of 1 hour in the 90° C bath. Do not exceed 5 hours.

**Note.**—Some aluminum vial caps have a center section that must be removed prior to placing into sample tray. If the cap is not removed, the injection needle will be damaged.

**8.2.2 Suspension Resin Slurry and Wet Cake Samples.** Decant the water from a wet cake sample, and turn the sample bottle upside down onto a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight ( $\pm 0.0001$  g). All samples must be prepressurized and then conditioned for 1 hour at 90° C. A sample of wet cake is used to

determine total solids (TS). This is required for calculating the RVC.

**8.2.3 Dispersion Resin Slurry and Geon Latex Samples.** The materials should not be filtered. Sample must be thoroughly mixed. Using a tared vial (tared, including septum and aluminum cap) add approximately eight drops (0.25 to 0.35 g) of slurry or latex using a medicine dropper. This should be done immediately after mixing. Seal the vial as soon as possible. Determine sample weight ( $\pm 0.0001$  g). After prepressurization, condition the vial for 1 hour at 90° C in the analyzer bath. Determine the TS on the slurry sample (Section 8.3.5).

**8.2.4 Inprocess Wastewater Samples.** Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight ( $\pm 0.0001$  g). Prepressurize the vial, and then condition for 1 to 2 hours as required at 90° C in the analyzer bath.

#### 8.3 Analysis.

**8.3.1 Preparation of Equipment.** Install the chromatographic column and condition overnight at 100° C. In the first operation, Porapak columns must be purged for 1 hour at 230° C.

Do not connect the exit end of the column to the detector while conditioning. Hydrogen and air to the detector must be turned off while the column is disconnected.

**8.3.1.1 Flow Rate Adjustments.** Adjust flow rates as follows:

a. **Nitrogen Carrier Gas.** Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to produce a flow rate of 30.0 cc/min. Accurately measure the flow rate at the exit end of the column using the soap film flowmeter and a stopwatch, with the oven and column at the analysis temperature. After the instrument program advances to the "B" (backflush) mode, adjust the nitrogen pressure regulator to exactly balance the nitrogen flow rate at the detector as was obtained in the "A" mode.

b. **Vial Prepressurizer Nitrogen.** After the nitrogen carrier is set, solve the following equation and adjust the pressure on the vial prepressurizer accordingly.

$$P = \frac{T_1}{T_2} \left[ P_1 - \frac{P_{w1} - P_{w2}}{7.50} \right] - 10 \text{ k Pa}$$

Where:

$T_1$  = Ambient temperature, °K.

$T_2$  = Conditioning bath temperature, °K.

$P_1$  = Gas chromatograph absolute dosing pressure (analysis mode), k Pa.

$P_{w1}$  = Water vapor pressure @ 90° C (525.8 mm Hg).

$P_{w2}$  = Water vapor pressure @ 22° C (19.8 mm Hg).

7.50 = mm Hg per k Pa.

10 k Pa = Factor to adjust the prepressurized pressure to slightly less than the dosing pressure.

Because of gauge errors, the apparatus may over-pressurize the vial. If the vial pressure is at or higher than the dosing pressure, an audible double injection will occur. If the vial

pressure is too low, errors will occur on resin samples because of inadequate time for head-space gas equilibrium. This condition can be avoided by running several standard gas samples at various pressures around the calculated pressure, and then selecting the highest pressure that does not produce a double injection. All samples and standards must be pressurized for 60 seconds using the vial prepressurizer. The vial is then placed into the 90° C conditioning bath and tested for leakage by placing a drop of water on the septum at the needle hole. A clean, burr-free needle is mandatory.

c. **Burner Air Supply.** Set regulator on cylinder to read 50 psig. Set regulator on chromatograph to supply air to burner at a rate between 250 and 300 cc/min. Check with bubble flowmeter.

d. **Hydrogen Supply.** Set regulator on cylinder to read 30 psig. Set regulator on chromatograph to supply approximately 35  $\pm$  5 cc/min. Optimize hydrogen flow to yield the most sensitive detector response without extinguishing the flame. Check flow with bubble meter and record this flow.

**8.3.1.2 Temperature Adjustments.** Set temperatures as follows:

a. **Oven (chromatograph column),** 140° C.

b. **Dosing Line,** 150° C.

c. **Injection Block,** 170° C.

d. **Sample Chamber, Water Temperature,** 90° C  $\pm$  1.0° C.

**8.3.1.3 Ignition of Flame Ionization Detector.** Ignite the detector according to the manufacturer's instructions.

**8.3.1.4 Amplifier Balance.** Balance the amplifier according to the manufacturer's instructions.

**8.3.2 Programming the Chromatograph.** Program the chromatograph as follows:

a. **I—Dosing or Injection Time.** The normal setting is 2 seconds.

b. **A—"Analysis Time."** The normal setting is approximately 70 percent of the VCM retention time. When this timer terminates, the programmer initiates backflushing of the first column.

c. **B—Backflushing Time.** The normal setting is double the "analysis time."

d. **W—Stabilization Time.** The normal setting is 0.5 min to 1.0 min.

e. **X—Number of Analyses Per Sample.** The normal setting is one.

**8.3.3 Preparation of Sample Turntable.** Before placing any sample into turntable, be certain that the center section of the aluminum cap has been removed. All samples and standards must be pressurized for 60 seconds by using the vial prepressurizer. The numbered sample vials should be placed in the corresponding numbered positions in the turntable. Insert samples in the following order:

Position 1 and 2—Old 2000-ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3—500-ppm standard, freshly prepared.

Position 4—500-ppm standard, freshly prepared.



Position 5—2000-ppm standard, freshly prepared.

Position 6—4000-ppm standard, freshly prepared.

Position 7—Sample No. 7 (This is the first sample of the day, but is given as 7 to be consistent with the turntable and the integrator printout.)

After all samples have been positioned, insert the second set of 50-, 500-, 2000-, and 4000-ppm standards. Samples, including standards, must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

8.3.4 Start Chromatograph Program. When all samples, including standards, have been conditioned at 90° C for 1 hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the dosing assembly.

8.3.5 Determination of TS. For wet cake, slurry, resin solution, and PVC latex samples, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110° C). Samples must be dried to constant weight. After first weighing, return the pan to the oven for a short period of time, and then reweigh to verify complete dryness. The TS are then calculated as the final sample weight divided by initial sample weight.

9. Calibration. Calibration is to be performed each 8-hour period when the instrument is used. Each day, prior to running samples, the column should be conditioned by running two 2000-ppm standards from the previous day.

9.1 Preparation of Standards. Calibration standards are prepared as follows: Place 100 µl or about two equal drops of distilled water in the sample vial, then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a ½-in. stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) for several minutes prior to filling the vials. After purging, reduce the flow rate to 500 to 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the ½-in. filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 90 seconds, during which time the filling tube is gradually slid to the top of the vial. After the 90 seconds, the tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations. The sealed vial must then be pressurized for 60 seconds using the vial prepressurizer. Test the vial for leakage by placing a drop of water on the septum at the needle hole.

9.2 Preparation of Chromatograph Calibration Curve.

Prepare two 50-, 500-, 2000-, and 4000-ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot  $A_n$ , the integrator area counts for each standard sample, versus  $C_n$ , the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

#### 10. Calculations.

10.1 Response Factor. If the calibration curve described in Section 9.2 passes through zero, a response factor,  $R_f$ , may be used to compute vinyl chloride concentrations. To compute a response factor, divide any particular  $A_n$  by the corresponding  $C_n$ .

$$R_f = \frac{A_s}{C_s} \quad \text{Eq. 107-1}$$

Where:

$A_n$  = Chromatograph area counts of vinyl

$$C_{rvc} = \frac{A_s P_a}{R_f T_1} \left[ \frac{M_v V_g}{R m} + K_p (TS) T_2 + K_w (1 - TS) T_2 \right] \quad \text{Eq. 107-2}$$

Results calculated using these equations represent concentration based on the total sample. To obtain results based on dry PVC content, divide by TS.

#### 11. References.

1. B.F. Goodrich, Residual Vinyl Chloride Monomer Content of Polyvinyl Chloride Resins, Latex, Wet Cake, Slurry and Water Samples. B.F. Goodrich Chemical Group Standard Test Procedure No. 1005-E. B.F. Goodrich Technical Center, Avon Lake, Ohio. October 8, 1979.
2. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS—Division of Polymer Chemistry, Polymer Preprints 15 (2):197, 1974.
3. Berens, A.R. The Diffusion of Vinyl Chloride in Polyvinyl Chloride. ACS—Division of Polymer Chemistry, Polymer

chloride for the sample.

$P_a$  = Ambient atmospheric pressure, mm Hg.  
 $R_f$  = Response factor in area counts per ppm VCM.

$T_1$  = Ambient laboratory temperature, °K.  
 $M_v$  = Molecular weight of VCM, 62.5 g/mole.

$V_g$  = Volume of the vapor phase, cm<sup>3</sup>.  
 $R$  = Gas constant, (62360 cm<sup>3</sup>) (mm Hg/mole) (°K).

$m$  = Sample weight, g.

$K_p$  = Henry's Law Constant for VCM in PVC @ 90° C,  $6.52 \times 10^{-6}$  g/g/mm Hg.

If the calibration curve does not pass through zero, the calibration curve must be employed to calculate each sample concentration unless the error introduced by using a particular  $R_f$  is known.

10.2 Residual Vinyl Chloride Monomer Concentration, ( $C_{rvc}$ ) or Vinyl Chloride Monomer Concentration. Calculate  $C_{rvc}$  in ppm or mg/kg as follows:

Preprints 15 (2):203, 1974.

4. Berens, A.R., L.B. Crider, C.J. Tomanek, and J.M. Whitney. Analysis for Vinyl Chloride in PVC Powders by Head-Space

TS = Total solids expressed as a decimal fraction.

$T_2$  = Equilibrium temperature, °K.

$K_w$  = Henry's Law Constant for VCM in water @ 90° C,  $7 \times 10^{-7}$  g/g/mm Hg.

Assuming the following conditions are met, these values can be substituted into Equation 107-2:

$P_a$  = 750 mm Hg.

$V_g$  = Vial volume—sample volume (Fisher vials are 22.0 cm<sup>3</sup> and Perkin-Elmer vials are 21.8 cm<sup>3</sup>).

$T_1$  = 23° C or 296° K.

$T_2$  = 90° C or 363° K.

$$C_{rvc} = \frac{A_s}{R_f} \frac{750}{296} \left[ \frac{65.5 \left( 21.8 - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9652} \right)}{62360 m} + 6.25 \times 10^{-6} (TS)(363) + 7.0 \times 10^{-7} (1-TS)(363) \right]$$

Gas Chromatography. Journal of Applied Polymer Science. 19:3169-3172, 1975.

5. Mansfield, R.A. The Evaluation of Henry's Law Constant ( $K_p$ ) and Water Enhancement in the Perkin-Elmer Multifract F-40 Gas Chromatograph. B.F. Goodrich. Avon Lake, Ohio. February 10, 1978.

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METHOD 110. DETERMINATION OF BENZENE  
FROM STATIONARY SOURCES

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to benzene, a carcinogen.

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of benzene in stack gases from processes as specified in the regulations. The method does not measure benzene contained in particulate matter.

1.2 Principle. An integrated bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

2. Range and Sensitivity

The range of this method is 0.1 to 70 ppm. The upper limit may be extended by extending the calibration range or by diluting the sample.

### 3. Interferences

The chromatograph columns and the corresponding operating parameters herein described normally provide an adequate resolution of benzene; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis problem, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique, such as analysis with a different column or GC/mass spectroscopy, and has the data available for review by the Administrator.

### 4. Apparatus

4.1 Sampling (see Figure 110-1). The sampling train consists of the following components:

4.1.1 Probe. Stainless steel, Pyrex\* glass, or Teflon tubing (as stack temperature permits), equipped with a glass wool plug to remove particulate matter.

4.1.2 Sample Lines. Teflon, 6.4-mm outside diameter, of sufficient length to connect probe to bag. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon completion of the test.

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\* Mention of any trade name or specific product does not constitute endorsement by the Environmental Protection Agency.

4.1.3 Quick Connects. Stainless steel, male (2) and female (2), with ball checks (one pair without), located as shown in Figure 110-1.

4.1.4 Tedlar or Aluminized Mylar Bags. 100-liter capacity, to contain sample.

4.1.5 Bag Containers. Rigid leakproof containers for sample bags, with covering to protect contents from sunlight.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump. Leak-free, with minimum of 2-liters/min capacity.

4.1.8 Charcoal Tube. To prevent admission of benzene and other organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liter/min.

4.1.10 Connecting Tubing. Teflon, 6.4-mm outside diameter, to assemble sampling train (Figure 110-1).

4.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, is required to connect bag to gas chromatograph sample loop for sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon conclusion of analysis of those bags.

4.3 Analysis. The following equipment is needed:

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder, and 1.0- to 2.0-ml sampling loop in

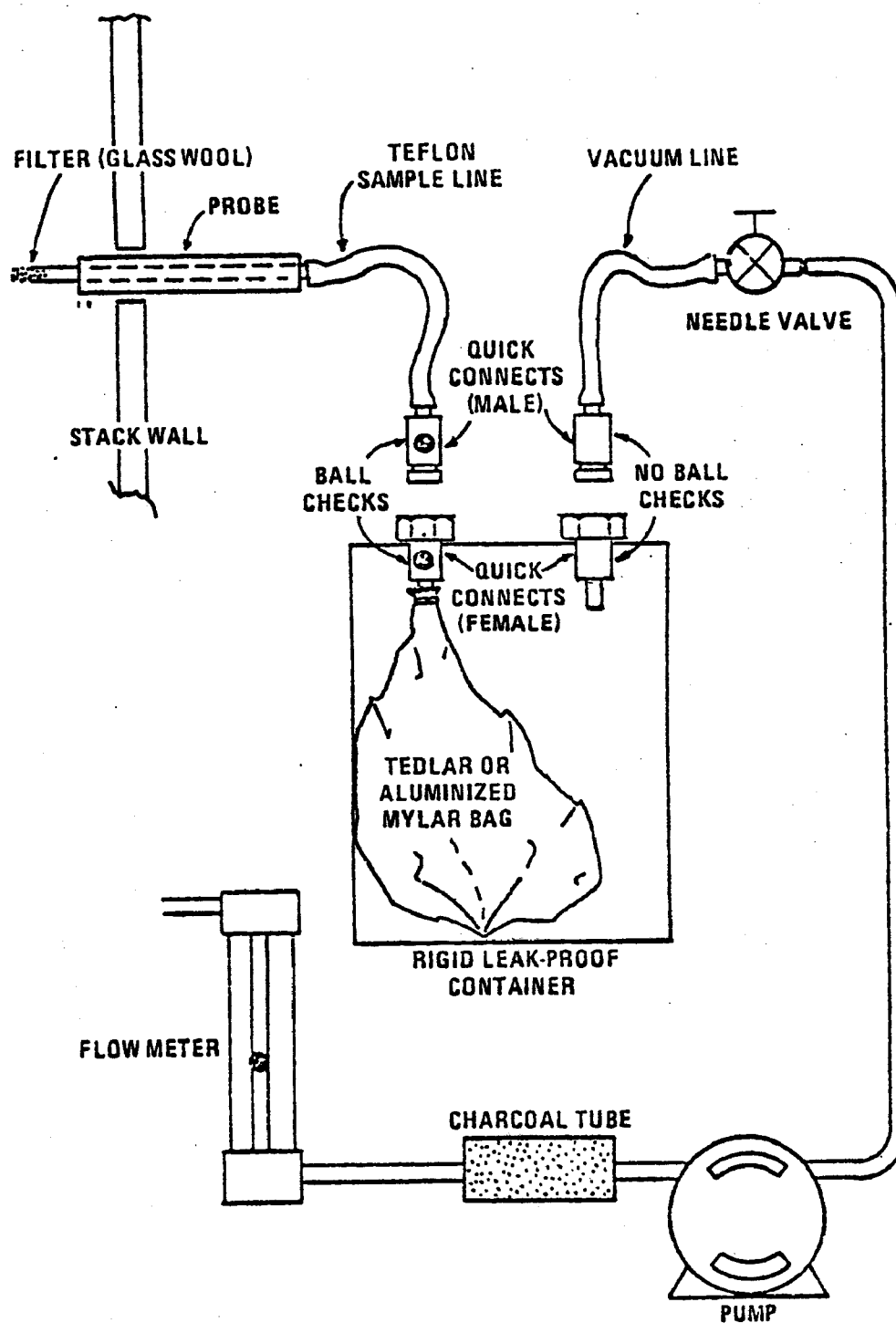


Figure 110-1. Integrated-bag sampling train. (Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1-ppm benzene that is at least as great as the average noise level. (Response is measured from the average value of the base line to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Columns. Columns as listed below. The analyst may use other columns provided that the precision and accuracy of the analysis of benzene standards are not impaired and he has available for review information confirming that there is adequate resolution of the benzene peak. (Adequate resolution is defined as an area overlap of not more than 10 percent of the benzene peak by an interferent peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromatographic Peak Resolution.")

4.3.2.1 Column A: Benzene in the Presence of Aliphatics. Stainless steel, 2.44 m by 3.2 mm, containing 10 percent 1,2,3-tris (2-cyanoethoxy) propane (TCEP) on 80/100 Chromasorb P AW.

4.3.2.2 Column B: Benzene with Separation of the Isomers of Xylene. Stainless steel, 1.83 m by 3.2 mm, containing 5 percent SP 1200/1.75 percent Bentone 34 on 100/120 Supelcoport.

4.3.3 Flow Meters (2). Rotameter type, 100-ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to 1°C, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump. Leak-free, with minimum of 100-ml/min capacity.

4.3.8 Recorder. Strip chart type, optionally equipped with either disc or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, on recorder, to measure chromatograph peak areas.

4.4 Calibration. Sections 4.4.2 through 4.4.5 are for the optional procedure in Section 7.1.

4.4.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringes. 1.0- $\mu$ l and 10- $\mu$ l, gas tight, individually calibrated to dispense liquid benzene.

4.4.4 Dry Gas Meter, with Temperature and Pressure Gauges. Accurate to  $\pm 2$  percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

4.4.5 Midget Impinger/Hot Plate Assembly. To vaporize benzene.

## 5. Reagents

Use only reagents that are of chromatographic grade.

5.1 Analysis. The following are needed for analysis:

5.1.1 Helium or Nitrogen. Zero grade, for chromatograph carrier gas.

5.1.2 Hydrogen. Zero grade.

5.1.3 Oxygen or Air. Zero grade, as required by the detector.

5.2 Calibration. Use one of the following options: either 5.1.1 and 5.2.2, or 5.2.3.

5.2.1 Benzene, 99 Mol Percent Pure. Certified by the manufacturer to contain a minimum of 99 Mol percent benzene; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (50-, 10-, and 5-ppm benzene in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph



calibration curve as described in Section 7.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of  $\pm 3$  percent or better (see Section 5.2.3.1). (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than  $\pm 5$  percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified benzene concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of benzene in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 50 and 100 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 5 and 10 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 Mol percent benzene) in accordance with the procedure described in Section 7.1 or by (b) having it analyzed by the National Bureau of Standards. The agreement between the initially determined concentration value and the verification concentration value must be within  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person supervising the analysis of samples. The audit cylinder standards shall be identically prepared as those in Section 5.2.3 (benzene in nitrogen cylinders). The concentrations of the audit cylinders should be: one low-concentration cylinder in the range of 5- to 20-ppm benzene, and one high-concentration cylinder in the range of 100- to 300-ppm benzene. When available, the tester may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711.

If audit cylinders are not available at the Environmental Protection Agency, the tester must secure an alternative source.

## 6. Procedure

6.1 Sampling. Assemble the sample train as shown in Figure 110-1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. 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 that will more than half fill the bag in the specified sample period. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. Then reposition the sampling and vacuum lines and begin the actual sampling, keeping the rate constant. At all times, 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. Protect the bag container from sunlight.

6.2 Sample Storage. Keep the sample bags out of direct sunlight. Perform the analysis within 4 days of sample collection.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve

to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 100-ml/min rotameter with flow control valve followed by a charcoal tube and a 1-in. H<sub>2</sub>O pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, always allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to 80°C for column A or 75°C for column B, and the detector temperature to 225°C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base-line drift has ceased. Purge the sample loop for 30 sec at the rate 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature,

carrier gas flow rate, chart speed, and the attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to benzene, as determined in Section 7.2.1. Measure the benzene peak area,  $A_m$ , by use of a disc integrator, electronic integrator, or a planimeter. Record  $A_m$  and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the benzene peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

6.5 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.)

## 7. Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance

### 7.1 Preparation of Benzene Standard Gas Mixtures.

(Optional Procedure--delete if cylinder standards are used.)

Assemble the apparatus shown in Figure 110-2. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure,

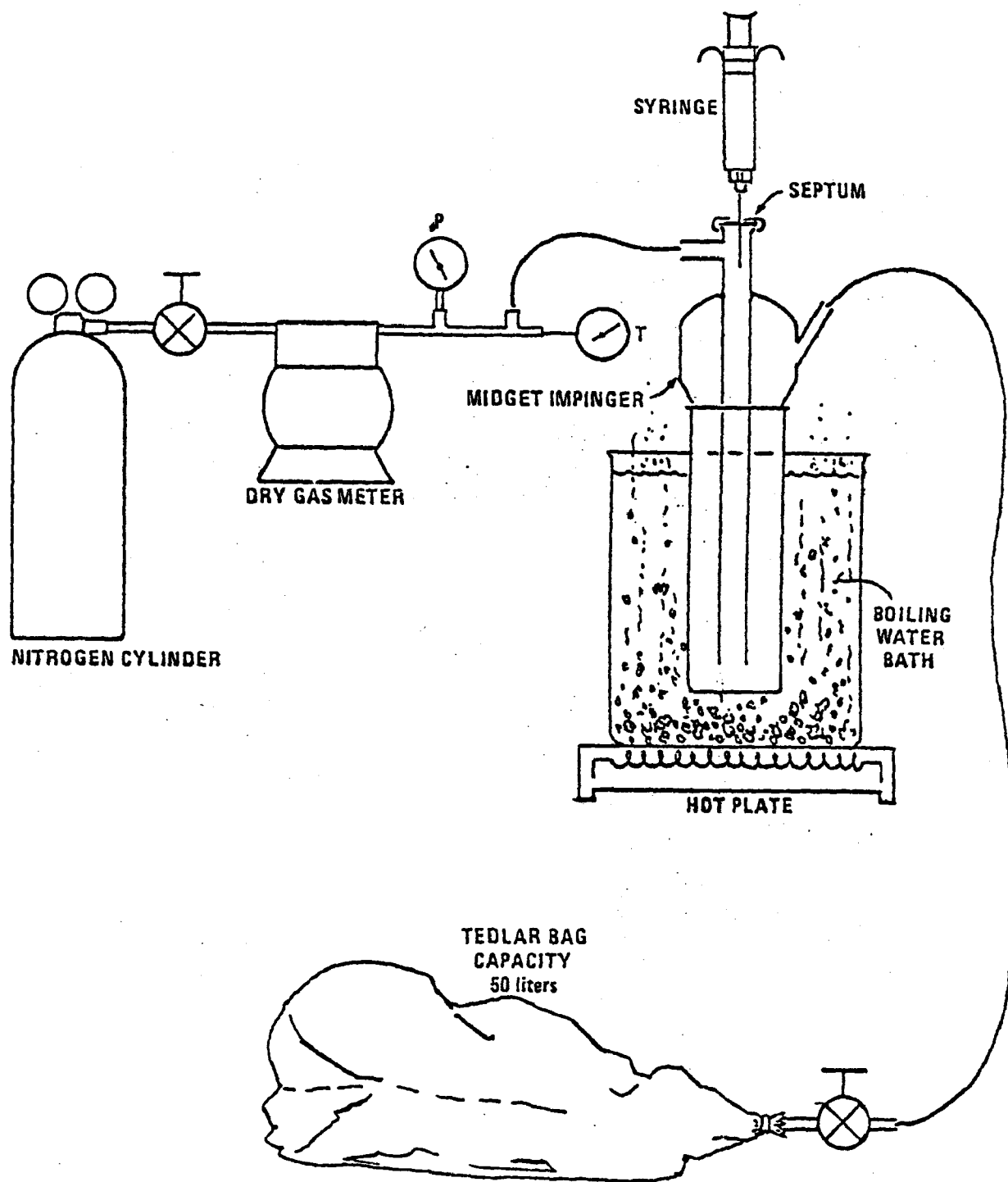


Figure 110-2. Preparation of standards (optional).

the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling use the 10- $\mu$ l syringe to inject 10  $\mu$ l of 99+ percent benzene through the septum on top of the impinger. This gives a concentration of approximately 50 ppm of benzene. In a like manner, use the other syringe to prepare dilutions having approximately 10- and 5-ppm benzene concentrations. To calculate the specific concentrations, refer to Section 8.1. These gas mixture standards may be used for 7 days from the date of preparation, after which time prepare new gas mixtures.

(Caution: If the new gas mixture standard is a lower concentration than the previous gas mixture standard, contamination may be a problem when a bag is reused.)

## 7.2 Calibration.

7.2.1 Determination of Benzene Retention Time. (This section can be performed simultaneously with Section 7.2.2.) Establish chromatograph conditions identical with those in Section 6.4 above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed, and the attenuator setting. Record peaks and detector responses that occur in the absence of benzene. Maintain conditions, with the equipment plumbing arranged identically to Section 6.3, and flush the sample loop

for 30 sec at the rate of 100 ml/min with one of the benzene calibration mixtures. Then activate the sample valve. Record the injection time. Select the peak that corresponds to benzene. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed, is defined as the benzene peak retention time. Since it is quite likely that there will be other organics present in the sample, it is very important that positive identification of the benzene peak be made.

#### 7.2.2 Preparation of Chromatograph Calibration Curve.

Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop 30 sec at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record  $C_c$ , the concentration of benzene injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the barometric pressure. Calculate  $A_c$ , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus  $C_c$ . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares



method. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

### 7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and before the sample analyses, perform the analysis audit described in Appendix E, Supplement B:

"Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required after bag use, it is also advised that it be performed before bag use. After each use, make sure a bag did not develop leaks by connecting a water manometer and pressurizing the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H<sub>2</sub>O (2 to 4 in. H<sub>2</sub>O) and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

## 8. Calculations

8.1 Optional Benzene Standards Concentrations. Calculate each benzene standard concentration ( $C_c$  in ppm) prepared in accordance with Section 7.1 as follows:

$$C_c = \frac{B(0.2706)(10^3)}{V_m Y \frac{293}{T_m} \frac{P_m}{760}}$$

$$= 701.9 \frac{B T_m}{V_m Y P_m} \quad \text{Eq. 110-1}$$

Where:

- B = Volume benzene injected,  $\mu\text{l}$ .
- $V_m$  = Gas volume measured by dry gas meter, liters.
- Y = Dry gas meter calibration factor, dimensionless.
- $P_m$  = Absolute pressure of the dry gas meter, mm Hg.
- $T_m$  = Absolute temperature of the dry gas meter,  $^{\circ}\text{K}$ .
- 0.2706 = Ideal gas volume of benzene at 293 $^{\circ}\text{K}$  and 760 mm Hg liters/ml.
- $10^3$  = Conversion factor [(ppm)(ml)]/ $\mu\text{l}$ .

8.2 Benzene Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of  $C_c$  that corresponds to  $A_c$ . Calculate the concentration of benzene in the sample ( $C_s$  in ppm) as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r (1 - S_{wb})} \quad \text{Eq. 110-2}$$

Where:

- $C_c$  = Concentration of benzene indicated by the gas chromatograph, ppm.
- $P_r$  = Reference pressure, the barometric pressure recorded during calibration, mm Hg.
- $T_i$  = Sample loop temperature at the time of analysis, °K.
- $P_i$  = Barometric pressure at time of analysis, mm Hg.
- $T_r$  = Reference temperature, the sample loop temperature recorded during calibration, °K.
- $S_{wb}$  = Water vapor content of the bag sample, volume fraction.

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## APPENDIX C - QUALITY ASSURANCE PROCEDURES

### PROCEDURE 1--DETERMINATION OF ADEQUATE CHROMATOGRAPHIC PEAK RESOLUTION

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from  $-2\sigma$  to  $+2\sigma$ . This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance,  $b$ , one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over the limits  $b-2\sigma_s$  to  $b+2\sigma_s$ , where  $\sigma_s$  is the standard deviation of the sample curve.

This calculation can be simplified in several ways. Overlap can be determined for curves of unit area; then actual areas can be introduced. Desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975, Texas Instruments, Inc., Dallas, Texas 75222.

$$\frac{1}{\sqrt{2\pi}\sigma_c} \int_{b-2\sigma_s}^{b+2\sigma_s} e^{\left(\frac{-t_c^2}{2\sigma_c^2}\right)} dt = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_s}{\sigma_c}}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx - \frac{1}{\sqrt{2\pi}} \int_{\frac{b+2\sigma_s}{\sigma_c}}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$$

The following calculation steps are required:\*

$$1. \quad 2\sigma_s = t_s / \sqrt{2 \ln 2}$$

$$2. \quad \sigma_c = t_c / 2\sqrt{2 \ln 2}$$

$$3. \quad x_1 = (b-2\sigma_s)/\sigma_c$$

$$4. \quad x_2 = (b+2\sigma_s)/\sigma_c$$

$$5. \quad Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$$

$$6. \quad Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$$

$$7. \quad I_o = Q(x_1) - Q(x_2)$$

$$8. \quad A_o = I_o A_c / A_s$$

$$9. \quad \text{Percentage overlap} = A_o \times 100 ,$$

where:

$A_s$  = Area of the sample peak of interest determined by electronic integration or by the formula  $A_s = h_s t_s$ .

$A_c$  = Area of the contaminant peak, determined in the same manner as  $A_s$ .

$b$  = Distance on the chromatographic chart that separates the maxima of the two peaks.

$H_s$  = Peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

---

\*In most instances,  $Q(x_2)$  is very small and may be neglected.

$t_s$  = Width of sample peak of interest at 1/2 peak height.

$t_c$  = Width of the contaminant peak at 1/2 of peak height.

$\sigma_s$  = Standard deviation of the sample compound of interest elution curve.

$\sigma_c$  = Standard deviation of the contaminant elution curve.

$Q(x_1)$  = Integral of the normal distribution function from  $x_1$  to infinity.

$Q(x_2)$  = Integral of the normal distribution function from  $x_2$  to infinity.

$I_o$  = Overlap integral.

$A_o$  = Area overlap fraction.

In judging the suitability of alternate GC columns or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for  $t_c$  as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

*Procedure 1—Determination of Adequate Chromatographic Peak Resolution*

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from  $-2\sigma$  to  $+2\sigma$ . This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance,  $b$ , one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compound overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over the limits  $b-2\sigma$ , to  $b+2\sigma$ , where  $\sigma$ , is the standard deviation of the sample curve.

This calculation can be simplified in several ways. Overlap can be determined for curves of unit area; then actual areas can be introduced. Desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975, Texas Instruments, Inc., Dallas, Texas 75222.

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$$\frac{1}{\sqrt{2\pi}\sigma_c} \int_{b-2\sigma_s}^{b+2\sigma_s} e^{\left(\frac{-t^2}{2\sigma_c^2}\right)} dt = \frac{1}{\sqrt{2\pi}} \int_{\frac{b-2\sigma_s}{\sigma_c}}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx - \frac{1}{\sqrt{2\pi}} \int_{\frac{b+2\sigma_s}{\sigma_c}}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$$

The following calculation steps are required:\*

1.  $2\sigma_s = t_s / \sqrt{2 \ln 2}$

2.  $\sigma_c = t_c / 2\sqrt{2 \ln 2}$

3.  $x_1 = (b-2\sigma_s)/\sigma_c$

4.  $x_2 = (b+2\sigma_s)/\sigma_c$

5.  $Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$

6.  $Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{\left(\frac{-x^2}{2}\right)} dx$

7.  $I_o = Q(x_1) - Q(x_2)$

8.  $A_o = I_o A_c / A_s$

9. Percentage overlap =  $A_o \times 100$ ,

where:

$A_s$  = Area of the sample peak of interest determined by electronic integration or by the formula  $A_s = h_s t_s$ .

$A_c$  = Area of the contaminant peak, determined in the same manner as  $A_s$ .

$b$  = Distance on the chromatographic chart that separates the maxima of the two peaks.

$H_s$  = Peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

$t_s$  = Width of sample peak of interest at 1/2 peak height.

$t_c$  = Width of the contaminant peak at 1/2 of peak height.

$\sigma_s$  = Standard deviation of the sample compound of interest elution curve.

$\sigma_c$  = Standard deviation of the contaminant elution curve.

$Q(x_1)$  = Integral of the normal distribution function from  $x_1$  to infinity.

$Q(x_2)$  = Integral of the normal distribution function from  $x_2$  to infinity.

$I_o$  = Overlap integral.

$A_o$  = Area overlap fraction.

In judging the suitability of alternate GC columns or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymmetric. In cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for  $t_s$  as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

\*In most instances,  $Q(x_2)$  is very small and may be neglected.

PROCEDURE 2--PROCEDURE FOR FIELD AUDITING GC ANALYSIS

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. The audit supervisor verifies that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism.

B. At the beginning and conclusion of the audit, the analyst records each cylinder number and pressure. An audit cylinder is never analyzed when the pressure drops below 200 psi.

C. During the audit, the analyst performs a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples, normally immediately after GC calibration and prior to sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analyst and compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within  $\pm 10$  percent, he directs the analyst to begin analyzing source samples. Audit supervisor judgment and/or supervisory policy determine action when agreement is not within  $\pm 10$  percent. When a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analysis, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor records each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited

must not under any circumstance be told actual audit concentrations until calculated concentrations have been submitted to the audit supervisor.

## FIELD AUDIT REPORT

PART A To be filled out by organization supplying audit cylinders

1. Organization supplying audit sample(s) and shipping address

\_\_\_\_\_

2. Audit supervisor, organization, and phone number

\_\_\_\_\_

\_\_\_\_\_

3. Shipping instructions: Name, Address, Attention

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

4. Guaranteed arrival date for cylinders \_\_\_\_\_

5. Planned shipping date for cylinders \_\_\_\_\_

6. Details on audit cylinders from last analysis

	Low Conc.	High Conc.
a. Date of last analysis	_____	_____
b. Cylinder number	_____	_____
c. Cylinder pressure, psi	_____	_____
d. Audit gas(es)/balance gas	_____	_____
e. Audit gas(es), ppm	_____	_____
f. Cylinder construction	_____	_____

**PART B** To be filled out by audit supervisor

1. Process sampled \_\_\_\_\_  
\_\_\_\_\_
2. Audit location \_\_\_\_\_  
\_\_\_\_\_
3. Name of individual audit \_\_\_\_\_
4. Audit date \_\_\_\_\_
5. Audit results

	Low Conc. Cylinder	High Conc. Cylinder
a. Cylinder number	_____	_____
b. Cylinder pressure before audit, psi	_____	_____
c. Cylinder pressure after audit, psi	_____	_____
d. Measured concentration, ppm		
Injection #1*	_____	_____
Injection #2*	_____	_____
Average	_____	_____
e. Actual audit concentration, ppm (Part A, 6e)	_____	_____
	_____	_____
f. Audit accuracy*		
Low Conc. Cylinder	_____	_____
High Conc. Cylinder	_____	_____

$$\text{*Percent accuracy} = \frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$$

- g. Problems detected (if any) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

\* Results of two consecutive injections that meet the sample analysis criteria of the test method.

**Procedure 2—Procedure for Field Auditing GC Analysis**

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

A. The audit supervisor verifies that audit cylinders are stored in a safe location both before and after the audit to prevent vandalism.

B. At the beginning and conclusion of the audit, the analyst records each cylinder number and pressure. An audit cylinder is never analyzed when the pressure drops below 200 psi.

C. During the audit, the analyst performs a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples, normally immediately after GC calibration and prior to sample analyses.

D. At the end of audit analyses, the audit supervisor requests the calculated concentrations from the analyst and compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within  $\pm 10$  percent, he directs the analyst to begin analyzing source samples. Audit supervisor judgment and/or supervisory policy determine action when agreement is not within  $\pm 10$  percent. When a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analysis, with a corrective factor to be applied to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy, as it may be misleading. The audit supervisor records each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told actual audit concentrations until calculated concentrations have been submitted to the audit supervisor.

**Field Audit Report**

**Part A.—To be filled out by organization supplying audit cylinders.**

1. Organization supplying audit sample(s) and shipping address \_\_\_\_\_

2. Audit supervisor, organization, and phone number \_\_\_\_\_

3. Shipping instructions: Name, Address, Attention \_\_\_\_\_

4. Guaranteed arrival date for cylinders \_\_\_\_\_

5. Planned shipping date for cylinders \_\_\_\_\_

6. Details on audit cylinders from last analysis \_\_\_\_\_

	Low conc.	High conc.
a. Date of last analysis _____		
b. Cylinder number _____		
c. Cylinder pressure, psi _____		
d. Audit gas(es)/balance gas _____		
e. Audit gas(es), ppm _____		
f. Cylinder construction _____		

**Part B.—To be filled out by audit supervisor.**

1. Process sampled \_\_\_\_\_

2. Audit location \_\_\_\_\_

3. Name of individual audit \_\_\_\_\_

4. Audit date \_\_\_\_\_

5. Audit results:

	Low conc. cylinder	High conc. cylinder
a. Cylinder number _____		
b. Cylinder pressure before audit, psi _____		
c. Cylinder pressure after audit, psi _____		
d. Measured concentration, ppm Injection #1* Injection #2* Average _____		
e. Actual audit concentration, ppm (Part A, 6e) _____		
f. Audit accuracy: <sup>1</sup> Low Conc. Cylinder _____ High Conc. Cylinder _____		

Percent <sup>1</sup> accuracy =  $\frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$

g. Problems detected (if any) \_\_\_\_\_

<sup>1</sup> Results of two consecutive injections that meet the sample analysis criteria of the test method.

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## Standard Test Method For DENSITY OF PAINT, VARNISH, LACQUER, AND RELATED PRODUCTS<sup>1</sup>

This standard is issued under the fixed designation D 1475; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval.

This method has been approved for use by agencies of the Department of Defense to replace Method 4184.1 of Federal Test Method Standard No. 141A and for listing in the DoD Index of Specifications and Standards.

NOTE—Editorial changes were made throughout in October 1980.

### 1. Scope

1.1 This method covers the measurement of density of paints, varnishes, lacquers, and components thereof, other than pigments, when in fluid form. It is particularly applicable where the fluid has too high a viscosity or where a component is too volatile for a specific gravity balance determination.

NOTE 1—The method provides for the maximum accuracy required for hiding power determinations. It is equally well suited for work in which less accuracy is required, by ignoring the directions for recalibration and consideration of temperature differences, by using the container as a "weight-per-gallon" cup.

### 2. Definition

2.1 *density*—the mass (weight in vacuo) of a unit volume of the liquid at any given temperature. In this method, it is expressed as the weight in grams per cubic millilitre, or as the weight, in pounds avoirdupois, of one U. S. gallon measure of the liquid at the specified temperature; in the absence of other temperature specification, 25°C is assumed.

### 3. Summary of Method

3.1 The accurately known absolute density of distilled water at various temperatures (Table 1) is used to calibrate the volume of a container. The weight of the paint liquid contents of the same container at a standard temperature (25°C) or at an agreed-upon temperature, is then determined, and density of the contents calculated in terms of grams per mil-

lilitre, or pounds per gallon at the specified temperature.

### 4. Apparatus

4.1 *Pycnometer*—Any type, or weight-per-gallon cup, having a capacity of from 20 to 100 mL may be used, provided that it may be filled readily with a viscous liquid, adjusted to exact volume, and covered to exclude loss of volatile matter.

4.2 *Thermometers*, graduated in 0.1°C, such as are supplied with glass pycnometers.

4.3 *Constant-Temperature Bath*, held at 25 ± 0.1°C is desirable.

4.4 *Laboratory Analytical Balance*.

NOTE 2—The usual weight-per-gallon cup and similar specialized pycnometers may have filled weights which exceed the capacity of the usual laboratory analytical balance. In such cases, use of a hanging pan, triple-beam balance, with scales graduated to 0.01 g has been found to provide results the mean of which was consistent with the overall precision and accuracy of the method.

4.5 *Desiccator and Desiccated Balance*, or a room of reasonably constant temperature and humidity are desirable.

### 5. Calibration of Pycnometer or Cup

5.1 Determine the volume of the container at the specified temperature by employing the following steps:

<sup>1</sup> This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials. Current edition approved Sept. 19, 1980. Originally issued 1957. Replaces D 1475 - 57 T.



5.1.1 Clean and dry the container and bring it to constant weight. Chromic acid (see 5.1.1.1) cleaner and nonresidual solvents may be used with glass containers, and solvents with metal containers. For maximum accuracy, rinsing, drying, and weighing must be continued until the difference between two successive weighings does not exceed 0.001 % of the weight of the container. Fingerprints on the container will change the weight and must be avoided. Record the weight,  $M$ , in grams.

5.1.1.1 Chromic acid cleaning solution is corrosive to skin, eyes and mucous membranes and can cause severe burns. Avoid contact with eyes, skin or clothing. In making dilute solution, always add acid to water with care. In case of contact, flush skin with water, using a shower if exposure is severe. Flush eyes for 15 minutes with copious amounts of water. Immediately call a physician. Remove clothing immediately and wash before reuse. Chromic acid cleaning solution is a strong oxidizer. Avoid contact with organic or reducing substances as a fire could result. See Supplier's Material Safety Data Sheet for further information.

5.1.2 Fill the container with freshly boiled distilled water at a temperature somewhat below that specified. Cap the container, leaving the overflow orifice open. Immediately remove excess overflowed water or water held in depressions by wiping dry with absorbent material. Avoid occluding air bubbles in the container.

5.1.3 Bring the container and contents to specified temperature. Use the constant-temperature bath or room if necessary. This will cause further slight flow of water from the overflow orifice due to the expansion of the water with the rise of the temperature.

5.1.4 Remove the excess overflow by wiping carefully with absorbent material, avoiding wicking of water out of orifice, and immediately cap the overflow tube where such has been provided. Dry the outside of the container, if necessary, by wiping with absorbent material. Do not remove overflow which occurs subsequent to the first wiping after attainment of the desired temperature (Note 3). Immediately weigh the filled container to the nearest 0.001 % of its weight (Note 4). Record this weight,  $N$ , in grams.

NOTE 3—Handling the container with bare hands will increase the temperature and cause more overflow from the overflow orifice, and will also leave fingerprints; hence, handling only with tongs and with hands protected by clean, dry, absorbent material is recommended.

NOTE 4—Immediate and rapid weighing of the filled container is recommended here to minimize loss of weight due to evaporation of the water through orifices, and from overflow subsequent to the first wiping after attainment of temperature where this overflow is not retained within a capped enclosure.

5.1.5 Calculate the container volume as follows:

$$v = (N - M)/q$$

where:

$v$  = volume of container, mL.

$N$  = weight of container and water, g (5.1.4).

$M$  = weight of dry container, g (5.1.1), and

$q$  = absolute density of water at specified temperature, g/mL (see Table 1).

5.1.6 Obtain the mean of at least three determinations of  $v$  to provide the value of  $V$  required in 6.2.

## 6. Procedure

6.1 Repeat the steps in Section 5, substituting the sample for the distilled water and a suitable nonresidual solvent for the acetone or alcohol (see 5.1.2 and Note 5). Record the weight of the filled container,  $W$ , and the weight of the empty container,  $w$ , in grams.

NOTE 5—Trapping of paint liquids in ground glass or metal joints is likely to result in high values of density which appear to increase with the viscosity and density of the material; such errors should be minimized by firm seating of the joints.

6.2 Calculate the density in grams per millilitre as follows:

$$D_m = (W - w)/V$$

where:

$D_m$  = density, g/mL.

6.3 Calculate the density in pounds per gallon as follows:

$$D = (W - w)K/V$$

where:

$D$  = density, lb/gal.

$K$  = 8.3455 (Note 6), and

$V$  = volume of container, mL (see 5.1.6).

NOTE 6—The factor  $K$ , 8.3455, is calculated from volume-weight relationship as follows:





## Standard Test Method for VOLATILE CONTENT OF COATINGS<sup>1</sup>

This standard is issued under the fixed designation D 2369; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of the last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This method has been approved for use by agencies of the Department of Defense to replace Method 4041.1 of Federal Test Method Standard No. 141A and for listing in the DoD Index of Specifications and Standards.*

### 1. Scope

1.1 This method describes two procedures for the determination of the weight percent volatile content of solvent reducible and water reducible coatings. Test specimens are heated at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 60 min, or optionally for 20 min. Although the technique used is the same, residence times in the oven differ. The two procedures are designated as follows:

1.1.1 *Procedure A*—Volatile Content of Coatings Determined for 20 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

1.1.2 *Procedure B (Preferred)*—Volatile Content of Coatings Determined for 60 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

1.1.2.1 Choice of and preference for 60 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$  as a general purpose method is based on the precision data presented in these methods that was obtained on both solvent reducible and water reducible coatings (see Section 7). These coatings (single package, heat cured) are commonly applied in factories to automobiles, metal containers, flat (coil) metal and large appliances and many other metal parts. Procedure B is presumed applicable, subject to further precision studies, to most kinds of paints and related coatings intended for either ambient or baking film formation, except where substantial amounts of volatiles may be consumed or produced in chemical reactions during film formation. If an oven residence time of 20 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$  is used the analyst must recognize that poorer precision was obtained using Procedure A (see Section 7).

NOTE 1—Testing at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 20 min was utilized for the establishment of the original method

in 1965. Precision data are not available and may not have been properly generated at the time. The nine paints tested then were all solvent reducible. These conditions, 20 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , are no longer satisfactory for the determination of volatile content of many coatings currently being listed in 1980. Water reducible and solvent reducible coatings were tested in the development of the present method at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$  for 60 min and 20 min for which precision data have been generated.

1.2 This method does not cover multi-package coatings wherein one or more parts may, at ambient conditions, contain liquid coreactants that are volatile until a chemical reaction has occurred with another component of the multi-package coating.

1.3 This method may not be applicable to all types of coatings such as printing inks, and other procedures may be substituted with mutual agreement of the producer and user. See Note 5.

### 2. Applicable Documents

#### 2.1 ASTM Standards:

- D 343 Specification for 2-Ethoxyethyl Acetate<sup>2</sup>
- D 362 Specification for Industrial Grade Toluene<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>1</sup>
- E 145 Specification for Gravity Convection

<sup>1</sup> These methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and are the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials.

Current edition approved June 26, 1981. Published September 1981. Originally published as D 2369 - 65 T. Last previous edition D 2369 - 80.

<sup>2</sup> Annual Book of ASTM Standards, Part 29.

<sup>3</sup> Annual Book of ASTM Standards, Parts 20, 21, 22, 24, 29, 30, 31, 37, 40, and 43.

and Forced-Ventilation Ovens<sup>4</sup>  
E 180 Recommended Practice for Developing Precision Data on ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>5</sup>

## 3. Apparatus

3.1 *Forced Draft Oven*, Type IIA or Type IIB as specified in Specification E 145.

3.2 *Syringe*, 5 mL, capable of dispensing the coating under test at sufficient rate that the specimen can be dissolved in the solvent (see 5.2).

3.3 *Weighing or Dropping Bottle*.

3.4 *Test Tube*, with new cork stopper.

3.5 *Aluminum Foil Dish*, 58 mm in diameter by 18 mm high with a smooth bottom surface. Precondition the dishes for 30 min in an oven at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$  and store in a desiccator prior to use.

## 4. Reagents

4.1 *Purity of Reagents*—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.<sup>6</sup> Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent grade water conforming to Specification D 1193.

4.3 *Toluene*, technical grade, Specification D 362.

4.4 *2-Ethoxyethyl Acetate*, technical grade, Specification D 343.

NOTE 2—The solvents and samples used in these methods may, under some conditions, be hazardous. Refer to the manufacturers Material Safety Data Sheet for specific handling and safety precautions. Safe laboratory handling procedures and all applicable U.S. Occupational Safety and Health Act regulations are to be followed in the handling of samples and solvents.

## 5. Procedure

5.1 Mix the sample, preferably on a mechanical shaker or roller, until homogeneous. If air

bubbles become entrapped, stir by hand until the air has been removed.

5.2 Using an appropriate weighing container (4.2, 4.3, or 4.4, with the syringe preferred for highest precision), weigh to 1 mg, by difference, a specimen of  $0.30 \pm 0.10$  g for coatings believed to have a volatile content less than 40 weight % or a specimen of  $0.50 \pm 0.10$  g for coatings believed to have a volatile content greater than 40 weight %, into a tared aluminum foil dish (4.5) into which has been added  $3 \pm 1$  mL of suitable solvent (3.1, 3.2 or 3.3). Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly prepare a duplicate.

NOTE 3—If the specimen cannot be dispersed in the solvents listed (3.1, 3.2 or 3.3) a compatible solvent may be substituted provided it is no less volatile than 2-ethoxyethyl acetate (3.3).

5.3 *Procedure A*—Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven (4.1) for 20 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

5.3.1 *Caution*—Provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

5.4 *Procedure B*—Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven (4.1) for 60 min at  $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ . *Caution*: See Section 5.3.1.

5.5 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature and weigh to 1 mg.

NOTE 5—If unusual decomposition or degradation of the specimen occurs during heating, the actual time and temperature used to cure the coating in practice may be substituted for the time and temperature specified in this method, subject to mutual agreement of producer and user.

## 6. Calculations

6.1 Calculate the percent volatile matter in

<sup>4</sup> *Annual Book of ASTM Standards*, Parts 39 and 41.

<sup>5</sup> *Annual Book of ASTM Standards*, Part 30.

<sup>6</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y. and the "United States Pharmacopeia."



the liquid coating as follows:

$$\text{Volatile matter, \%} = 100 - [(W_2 - W_1)/S] \times 100\}$$

where:

$W_1$  = weight of dish.

$W_2$  = weight of dish plus specimen after heating, and

$S$  = weight of specimen.

6.2 The percent of nonvolatile matter in the coating may be calculated by difference as follows:

$$\text{Nonvolatile matter} = 100 - \text{volatile matter}$$

## 7. Precision

### 7.1 Procedure A (20 min at $110^\circ\text{C} \pm 5^\circ\text{C}$ ):

7.1.1 The precision estimates are based on an interlaboratory study<sup>7</sup> in which one operator in each of 15 laboratories analyzed in duplicate on two different days seven samples of water-based paints and eight samples of solvent-based paints containing between 35 % and 72 % volatile material. The paints were commercially supplied. The results were analyzed statistically in accordance with Recommended Practice E 180, and the within-laboratories coefficient of variation was found to be 1.1 % relative at 193 degrees of freedom and the between-laboratories coefficient of variation was 2.5 % relative at 178 degrees of freedom. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95% confidence level.

7.1.1.1 *Repeatability*—Two results each the mean of duplicate determinations, obtained by the same operator on different days, should be considered suspect if they differ by more than 2.9% relative.

7.1.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 7.1% relative.

### 7.2 Procedure B (60 min at $110^\circ\text{C} \pm 5^\circ\text{C}$ ):

7.2.1 The precision estimated for tests at 60 min at  $110^\circ\text{C} \pm 5^\circ\text{C}$  are based on an interlaboratory study<sup>7</sup> in which one operator in each of 15 laboratories analyzed in duplicate on two different days seven samples of water-based paints and eight samples of solvent-based paints containing between 35 % and 72 % volatile material. The paints were commercially supplied. The results were analyzed statistically in accordance with Recommended Practice E 180, and the within-laboratories coefficient of variation was found to be 0.5 % relative at 213 degrees of freedom and the between-laboratories coefficient of variation was 1.7 % relative at 198 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

7.2.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 1.5 % relative.

7.2.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 4.7 % relative.

<sup>7</sup> Supporting data are available on loan from ASTM Headquarters, 1916 Race St., Philadelphia, Pa. 19103. Request RR:D01 - 1026.

*The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.*



## Standard Test Method for WATER CONTENT OF WATER-REDUCIBLE PAINTS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH<sup>1</sup>

This standard is issued under the fixed designation D 3792; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

<sup>1</sup> NOTE—Section 4.3.1 was editorially changed in October 1982.

### 1. Scope

1.1 This method is for the determination of total water content of water-reducible paints. It has been evaluated for emulsion systems (styrene-butadiene, poly(vinylacetate)-acrylic, acrylic). It has not yet been evaluated for other water-reducible paints but is believed to be applicable. The established working range of this method is from 40 to 55 % water. There is no reason to believe that it will not work outside of this range.

### 2. Applicable Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 1364 Test for Water in Volatile Solvents<sup>2</sup>

E 180 Recommended Practice for Developing Precision Data on ASTM Methods for Analysis and Testing of Industrial Chemicals,<sup>3</sup>

E 260 Recommended Practice for General Gas Chromatographic Procedures<sup>3</sup>

### 3. Summary of Method

3.1 A suitable aliquot of whole paint is internally standardized with anhydrous 2-propanol, diluted with dimethylformamide, and then injected onto a gas chromatographic column containing a porous polymer packing that separates water from other volatile components. The water content is determined from area calculations of the materials producing peaks on the chromatogram.

### 4. Apparatus

4.1 *Gas Chromatograph*—Any instrument equipped with a thermal conductivity detector

may be used. Temperature programming capability is preferable, but isothermal operations may be adequate. See Table 1.

4.2 *Recorder*—A 1-10-mV recorder with a full-scale response time of 2 s or less and a maximum noise of  $\pm 0.03$  % of full scale.

4.3 *Column*—The column should be 1.22 m long by 3.2-mm outside diameter stainless steel, or other suitable material, packed with 60/80 mesh (180 to 250  $\mu$ m) porous polymer packing material.<sup>4</sup> A replaceable glass sleeve, glass wool plug, or other suitable material may be placed on the entrance end of the column to retain any nonvolatile materials. This will minimize sludge build-up in the column.

4.3.1 *Column Conditioning Procedure*—The packed column is installed in the gas chromatographic unit leaving the exit end disconnected from the detector. This will prevent any contamination of the detector with the column bleed. Set the helium or nitrogen flow rate at 20 to 30 ml/min if a  $\frac{1}{8}$ -in. (3.2-mm) outside diameter column is used. Purge the column 5 or 10 min before heating. Heat the column from room temperature to 200°C at 5°C/min and hold this temperature for at least 12 h

<sup>1</sup> This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials.

Current edition approved May 25, 1979. Published July 1979.

<sup>2</sup> Annual Book of ASTM Standards, Part 29.

<sup>3</sup> Annual Book of ASTM Standards, Part 42.

<sup>4</sup> Porapak Q® is a trademark of Waters Associates, Inc., Milford, Mass. and has been found satisfactory. Porapak Q® is available from Waters Associates and most gas chromatographic supplies distributors, such as Anspec Co., P. O. Box 44, Ann Arbor, Mich., or Supelco Inc., Bellefonte, Pa.

(overnight). At the end of this period of time, heat the column to 250°C (the maximum temperature for this packing) at a 5°C/min rate and hold at this temperature for several hours. Cool the column to room temperature and connect the column detector. Reheat the column to 250°C at 5°C/min to observe if there is column bleed. Optimum conditioning of this column may take several cycles of the heating program before a good recorder baseline is achieved.

## 5. Reagents and Materials

**5.1 Purity of Reagents**—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.<sup>3</sup> 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 Purity of Water**—Unless otherwise indicated, reference to water shall be understood to mean Type II reagent water conforming to Specification D 1193.

**5.3 Carrier Gas**—Helium of 99.995 % or higher purity. High-purity nitrogen may also be used.

**5.4 Dimethylformamide (DMF) (Anhydrous)** gas chromatography, spectrophotometric quality (See Note 1).

**5.5 Liquid Charging Devices**, such as microsyringes of 10 or 25- $\mu$ l capacity.

**5.6 2-Propanol (Anhydrous)**—See Note 1.

**5.7 Septum Sample Vials**, 10-ml capacity with fluorocarbon-faced septa are preferred.

**NOTE 1**—The water content of the 2-propanol and dimethyl formamide should be determined by Karl Fischer Titration (Method D1364) prior to use. Anhydrous 2-propanol must be used; if water is found by Karl Fischer titration the 2-propanol must be replaced or dried prior to use.

## 6. Safety Precaution

**6.1 Dimethylformamide** is harmful if inhaled or absorbed through skin. Use only with adequate ventilation. Avoid contact with skin, eyes, and clothing. In case of contact, immediately flush skin or eyes with plenty of water for at least 15 min. If eyes are affected, call a physician. Remove and wash clothing before reuse.

**6.2 2-Propanol** is flammable. Its vapor is harmful especially to the eyes. Use with adequate ventilation. Avoid contact with skin and eyes. In case of contact with liquid, wash skin with soap and water. For eye contact with high concentration of vapor or liquid, flush eyes for 15 min and see a physician immediately. Remove contaminated clothing immediately.

## 7. Calibration

**7.1** Before each calibration and series of determinations (or daily) condition the column at 200°C for 1 h with carrier gas flow.

**7.2 Determination of Relative Response Factors**—Anhydrous 2-propanol is used as an internal standard. The response factor to water relative to the standard is determined by means of the following procedure. See Fig. 1 for a typical chromatogram. It is good practice to determine the response factor daily or with each series of determinations.

**7.2.1** Weigh about 0.2 g of water and 0.2 g of 2-propanol to the nearest 0.1 mg into a septum sample vial. If it has been determined that a correction for the water content is necessary, weigh 2 ml of dimethyl formamide into the vial. If the dimethylformamide is anhydrous, simply add 2 ml of it as weighing is not necessary.

**7.2.2** Inject a 1  $\mu$ l aliquot of the above solution onto the column and record the chromatogram. The retention order and approximate retention times after the air peak are (1) water, about 0.7 min; (2) 2-propanol, about 2.8 min, and (3) DMF, about 7 min.

**7.2.3** The preferred procedure to obtain the water content of the DMF is by Karl Fischer titration (Note 1). If this has been done, calculate the response factor for water by means of the following equation:

$$R = \frac{W_1 A_{H_2O}}{(W_{H_2O} + P W_1) A_1}$$

where:

$R$  = response factor,

$W_1$  = weight of 2-propanol.

$W_{H_2O}$  = weight of water added.

<sup>3</sup> "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, D. C. For suggestion on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards" by Joseph R. Ivin, D. Van Nostrand Co., Inc., New York, N. Y. and the "United States Pharmacopeia."

$W_s$  = weight of dimethyl formamide.  
 $A_{H_2O}$  = area of water peak,  
 $A_i$  = area of 2-propanol peak, and  
 $P$  =  $\frac{\text{weight \% water in DMF}}{100}$

7.2.4 If Karl Fischer titration is not available, the following procedure may be used to obtain a reasonable estimate of the response factor:

7.2.4.1 Inject the same size aliquot of DMF and 2-propanol mixture, but without added water, as a blank. Note the area of the water peak in the blank.

7.2.4.2 The response factor for water is calculated by means of the following equation:

$$R = \frac{W_i(A_{H_2O} - B)}{W_{H_2O}A_i}$$

where:

$R$  = response factor,  
 $W_i$  = weight of 2-propanol,  
 $W_{H_2O}$  = weight of the water,  
 $A_i$  = area of 2-propanol peak,  
 $A_{H_2O}$  = area of the water peak, and  
 $B$  = area of the water peak the blank.

## 8. Procedure

8.1 Weigh to the nearest 0.1 mg 0.6 g of water-reducible paint (see Note 2) and 0.2 g of 2-propanol into a septum vial. Add 2-ml of dimethylformamide into the vial. Seal the vial. Prepare a blank containing the 2-propanol and dimethylformamide but no paint.

NOTE 2—Check each paint system to be analyzed for interfering peaks. Coalescing agents do not interfere with this determination.

8.2 Shake the vials on a wrist action shaker or other suitable device for 15 min. To facilitate settling of solids allow the samples to stand for 5 min just prior to injection into the chromatograph. Low speed centrifugation may also be used.

8.3 Inject a 1  $\mu$ l sample of the supernatant from the prepared solutions onto the chromatographic column. Record the chromatograms using the conditions described in Table 1.1.

## 9. Calculations

9.1 Measure the area of the water peak and the 2-propanol internal standard peak and multiply each area by the appropriate attenuation factor to express the peak areas on a common

basis. Use of an electronic integrator is recommended to obtain the best accuracy and precision. However, triangulation, planimeter, paper cut out, or ball and disk integrator may be used.

9.2 Determine the water concentration in the paint by means of the following equation:

$$H_2O, \% = \frac{A_{H_2O} \times W_i \times 100}{A_i \times W_p \times R}$$

where:

$A_{H_2O}$  = area of water peak,  
 $A_i$  = area of 2-propanol peak,  
 $W_i$  = weight of 2-propanol added,  
 $W_p$  = weight of paint, and  
 $R$  = response factor determined in 7.2.

## 9.3 Correction for Water Content of Solvent:

9.3.1 If the blank indicates the presence of a detectable peak for water in the dimethylformamide used as solvent, make a correction in the calculation.

9.3.2 To make the correction, the water content of the dimethyl formamide is determined either by chromatography (7.2.4) or, preferably, by Karl Fischer titration (7.2). Calculate the water content due to the solvent by using the following equation:

$$H_2O(S), \% = \frac{(W_s)(P)100}{W_p}$$

where:

$W_s$  = weight of dimethylformamide,  
 $W_p$  = weight of paint, and  
 $P$  =  $\frac{\text{weight \% water in DMF}}{100}$ .

9.3.3 The water content of the paint in this case is the difference between the total percent determined in 9.2 and the correction for the solvent water content as determined in 9.3.2.

## 10. Precision\*

10.1 The precision estimates are based on an interlaboratory study in which nine different laboratories analyzed in duplicate, on two different days four samples of water based emulsion paints containing from 40 to 55 %  $H_2O$  (theoretical). The results obtained were analyzed statistically in accordance with Recommended Practice E 180. The within laboratory coefficient of variation was found to be 1.0 %

\* Data supporting the precision statements are available from the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa 19103 as RR. D01-1022.



relative at 34 degrees of freedom and the between laboratory coefficient of variation was 2.6 % relative at 30 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

10.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by

the same operator on different days, should be considered suspect if they differ by more than 2.9 % relative.

10.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories, should be considered suspect if they differ by more than 7.5 % relative.

TABLE 1 Instrument Parameters (Typical Conditions)<sup>A</sup>

Detector	thermal conductivity
Column	1.22 m by 3.2-mm outside diameter packed with 60 to 80 mesh porous polymer packing <sup>a</sup>
Temperatures:	
Sample inlet	200°C
Detector	240°C
Column	
Initial	80°C
Final	170°C
Program rate	30°C/min
Carrier Gas	helium or nitrogen
Flow rate	50 ml/min
Detector current	150 mA
Specimen size	1 µl

<sup>A</sup> For isothermal operation set the column temperature at 140°C. After the 2-propanol has cleared the column adjust the temperature to 170°C until DMF clears the column. Reset the temperature to 140°C for subsequent runs.

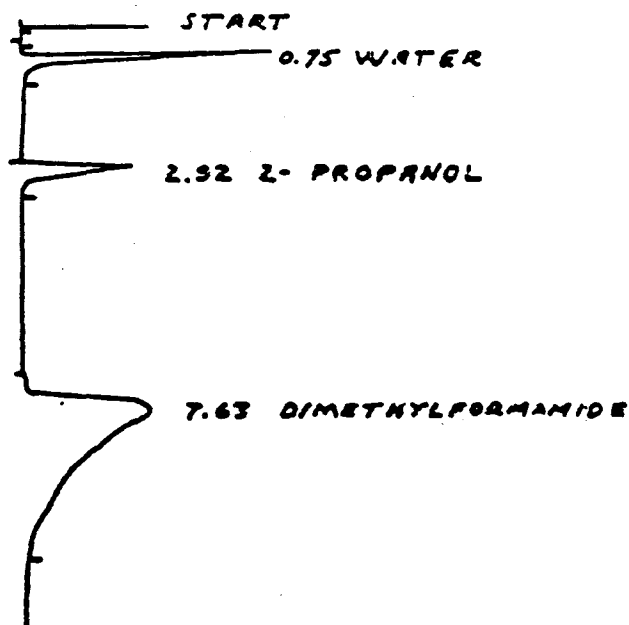


FIG. 1 Typical Chromatogram.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.





## Standard Test Method for WATER IN PAINTS AND PAINT MATERIALS BY KARL FISCHER METHOD<sup>1</sup>

This standard is issued under the fixed designation D 4017; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This method is applicable to all paints and paint materials, including resins, monomers, and solvents, with the exception of aldehydes and certain active metals, metal oxides and metal hydroxides. While the evaluation was limited to pigmented products containing amounts of water in the 30 to 70 % range, there is reason to believe that higher and lower concentrations can be determined by this method.

### 2. Applicable Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

E 180 Recommended Practice For Developing Precision Data on ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

E 203 Test for Water Using Karl Fischer Reagent<sup>3</sup>

#### 2.2 Other Document:

Archer, E. E. and Jeeter, H. W., *Analyst*, Vol. 90, 1965, p. 357.

### 3. Summary of Method

3.1 The material is dissolved in pyridine, or another appropriate solvent, and titrated directly with standardized Karl Fischer Reagent, to an electrometric end point. The sluggish reaction with water in pyridine is accelerated with a chemical catalyst, 1-ethylpiperidine.

3.2 Pyridine is used as a solvent to minimize interference problems caused by ketones. It is also used because the more common solvent, methanol, will not dissolve many common resins and because methanol reacts with some resins to produce water.

### 4. Apparatus

4.1 *Karl Fischer Apparatus*, manual or automatic, encompassed by the description in Method E 203. Apparatus should be equipped with a 25-mL buret, Class A, or equivalent.

4.2 *Syringe*, 100- $\mu$ L capacity, with needle.

4.3 *Syringes*, 1-mL and 10-mL capacity, without needle, but equipped with caps.

### 5. Reagents

5.1 *Purity of Reagents*—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.<sup>4</sup> Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent grade water conform-

<sup>1</sup> This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials.

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<sup>2</sup> *Annual Book of ASTM Standards*, Parts 20, 21, 22, 26, 29, 31, 40, and 43.

<sup>3</sup> *Annual Book of ASTM Standards*, Part 30.

<sup>4</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y. and the "United States Pharmacopeia."



ing to Specification D 1193.

5.3 *Karl Fischer Reagent*.<sup>5</sup>

5.4 *Pyridine*, reagent grade.<sup>6</sup>

5.5 *1-Ethylpiperidine*.<sup>6</sup>

## 6. Safety Precautions

6.1 Karl Fischer reagent contains four toxic compounds, namely iodine, sulfur dioxide, pyridine, and methanol or glycol ether. The reagent should be prepared and dispensed in a hood. Care must be exercised to avoid inhalation or skin contact. Following accidental contact or spillage, wash with large quantities of water.

6.2 Pyridine and methanol solvents should be treated with the same care as Karl Fischer reagent.

6.3 1-ethylpiperidine is of unknown toxicity and, therefore, should be handled with the same care as the above materials.

6.4 Many paint materials are highly flammable and should be transferred in a well-ventilated area free from sources of ignition.

## 7. Procedure

### 7.1 *Standardization of Karl Fischer Reagent:*

7.1.1 Add enough fresh pyridine to cover the electrode tip, plus 1 mL of 1-ethylpiperidine catalyst per 20 mL of pyridine. Catalyst performs best at a concentration of about 5 % of the volume present.

7.1.2 Fill the 100- $\mu$ L syringe to about half full with distilled water and weigh to the nearest 0.1 mg.

7.1.3 Pretitrate the pyridine to the endpoint indicated by the equipment manufacturer, by adding just enough Karl Fischer Reagent I (hereafter referred to as KFR) to cause the endpoint to hold for at least 30 s.

7.1.3.1 The use of the catalyst greatly increases the reaction rate between water and Karl Fischer reagent. To obtain reliable results, increase the electrode sensitivity and reduce titration rate to a minimum. Most instruments have controls for these functions. Consult instructional manual for information on these controls.

7.1.4 Empty the contents of the syringe into the titrator vessel. Immediately replace the stopper of the sample port and titrate with KFR to the endpoint as described in 7.1.3.

7.1.5 Repeat standardization until replicate

values of  $F$  agree within 1 %. Determine the mean of at least two such determinations. Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

### 7.1.6 *Calculation:*

$$F = J/P$$

where:

$F$  = KFR titre,

$J$  = water added, g, and

$P$  = KFR used, mL.

The value for  $F$  should be recorded to the four significant digits and should be the mean of at least two determinations. Typical values are in the range of 0.004000 to 0.006000 g/mL.

### 7.2 *Analysis of Samples With More Than 0.5 % Water:*

7.2.1 The titration vessel should already contain pretitrated pyridine and catalyst, as described in steps 7.1.1 and 7.1.3 in the standardization procedure. Best results are obtained with fresh solvent, that is, contain no previously titrated specimen in the vessel.

7.2.2 With a 1-mL or 10-mL syringe, draw the amount of material indicated in Table I.

7.2.2.1 Remove the syringe from the sample, pull the plunger out a little further, wipe the excess material off the syringe, and place a cap on the syringe tip. Weigh the filled syringe to the nearest 0.1 mg.

7.2.3 Remove the cap, and empty the syringe contents into the pretitrated pyridine vessel. Pull the plunger out and replace the cap. Titrate the specimen with KFR to the endpoint described in 7.1.3.

7.2.4 Reweigh the emptied syringe, and calculate the specimen weight by difference.

### 7.2.5 *Calculation:*

% water = (millilitres KFR used

$$\times F \times 100)/(\text{grams sample})$$

### 7.3 *Analysis of Materials With Less Than 0.5 % Water:*

7.3.1 For 0.1 to 0.5 %, follow procedure in 7.2 (1-g specimen), except substitute a 1-mL microburet for the 25-mL buret in the Karl Fischer apparatus.

7.3.2 For less than 0.1 %, use a 1-mL micro

<sup>5</sup> Fischer Scientific Co. Su-K-3 or equivalent has been found suitable.

<sup>6</sup> Available from most suppliers of laboratory chemicals.

buret and increase specimen size as much as needed, up to 10 g. It should be possible to measure moisture levels down to 1 ppm (0.0001 %) by this approach (see Note).

NOTE—Specimens with less than 0.1 % water may require special handling techniques to prevent pickup of atmospheric moisture. The precision of this test was determined with specimens containing higher water levels.

## 8. Maintenance

8.1 *Cleanup*—Clean the titration vessel by rinsing with fresh pyridine. Do not use methanol or other solvents.

8.2 *Dryness*—Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace dessicant when indicator color changes through *half of the tube*.

8.3 *Electrode Performance*—If electrode response is sluggish or otherwise off standard, take the following steps, in turn, to correct the problem. Test the electrode with a titration after each step, to determine if the next step is required.

8.3.1 Wipe the electrode tip with a clean paper towel.

8.3.2 Wash the electrode by dipping in concentrated hydrochloric acid for at least 1 min. Rinse first with distilled water, then with methanol.

8.3.3 Follow manufacturer's instructions on

resetting endpoint meter.

8.3.4 Replace power source. See manual for replacement procedure.

8.3.5 Replace the electrode.

## 9. Precision

9.1 The precision estimates are based on an interlaboratory study in which one operator in each of seven different laboratories analyzed in duplicate, on two different days, seven samples of water-based paints of various types containing between 25 to 75 % water. The results were analyzed statistically in accordance with Recommended Practice E 180. The within-laboratories' coefficient of variation was found to be 1.7 % relative at 98 degrees of freedom, and the between-laboratories' coefficient of variation was 5.3 % relative, at 42 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

9.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 4.7 % relative.

9.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 15.0 % relative.

TABLE 1 Specimen Guidelines

Expected water, %	Approximate Specimen Weight, g	Approximate Ti- trant Volume at 5 mg/mL titre, mL
0.5-1.0	5	5-10
1-3	2-5	10-20
3-10	1-2	10-20
10-30	0.4-1.0	20-25
30-70	0.1-0.4	15-25
>70	0.1	20

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