

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25

check for contamination. Treat the gas cylinders as noncondensable gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH₄, CO, CO₂, or NMO. The total concentration must be less than 5 ppm.

10.1.1.2 Oxidation Catalyst Efficiency Check.

10.1.1.2.1 With a clean condensate trap installed in the recovery system or a $\frac{1}{8}$ " stainless steel connector tube, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 7.4.1). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow-control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

10.1.1.2.2 After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow-control valve. Keep the flow adjusted such that the pressure in the system is maintained within 10 percent of atmospheric pressure. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO₂ using the NMO analyzer; the catalyst efficiency is acceptable if the CO₂ concentration is within 2 percent of the methane standard concentration.

10.1.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 25-7. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O₂ flow rates to normal operating levels. Attach an evacuated ICV 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 sections 10.1.1.3.1 to 10.1.1.3.4) into the injection port. Operate the trap recovery system as described in section 11.1.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO₂ concentration. For each injection, calculate the percent recovery according to section 12.7. Calculate the relative standard deviation for each set of triplicate injections according to section 12.8. The performance test is acceptable if the average percent recovery is 100 \pm 5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 μ l hexane.

- 10.1.1.3.2 10 μ l hexane.
- 10.1.1.3.3 50 μ l decane.
- 10.1.1.3.4 10 μ l decane.

10.1.2 NMO Analyzer. Perform these tests before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

10.1.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 7.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

10.1.2.2 Reduction Catalyst Efficiency Check. With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (Section 7.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.1.2.3 NMO Analyzer Linearity Check Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 7.4.2. Make triplicate injections of each calibration gas. For each gas (*i.e.*, each set of triplicate injections), calculate the average response factor (area/ppm C) for each gas, as well as the relative standard deviation (according to section 12.8). Then calculate the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation gas is less than 2 percent of the overall mean value. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}). Repeat the linearity check using the CO₂ standards specified in section 7.4.3. Make triplicate injections of each 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. Record the overall mean of the response factor values as the CO₂ calibration response factor (RF_{CO₂}). The RF_{CO₂} must be within 10 percent of the RF_{NMO}.

10.1.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 7.4.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 percent of the expected value.

10.2 NMO Analyzer Daily Calibration. The following calibration procedures shall be performed before and immediately after the

Pt. 60, App. A-7, Meth. 25

40 CFR Ch. I (7-1-17 Edition)

analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO₂ Response Factor. Inject triplicate samples of the high level CO₂ calibration gas (Section 7.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF_{CO₂} calculated during the initial performance test (Section 10.1.2.3). Use the daily response factor (DRF_{CO₂}) for analyzer calibration and the calculation of measured CO₂ concentrations in the ICV samples.

10.2.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder gas (Section 7.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 10 percent of the RF_{NMO} calculated during the initial performance test (Section 10.1.2.4). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

10.3 Sample Tank and ICV Volume. The volume of the gas sampling tanks used must be determined. Determine the tank and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedure

11.1 Condensate Recovery. See Figure 25-9. Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

11.1.1 Daily Performance Checks. Each day before analyzing any samples, perform the following tests:

11.1.1.1 Leak-Check. With the carrier gas inlets and the sample recovery valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

11.1.1.2 System Background Test. Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 cc/min and 150 cc/min, respectively, with the sample recovery valve in vent position. Using a 10-ml syringe, withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO₂ content. The system background is acceptable if the CO₂ concentration is less than 10 ppm.

11.1.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in section 10.1.1.2. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

11.1.2 Condensate Trap CO₂ Purge and Sample Tank Pressurization.

11.1.2.1 After sampling is completed, the condensate trap will contain condensed water and organics and a small volume of sampled gas. This gas from the stack may contain a significant amount of CO₂ which must be removed from the condensate trap before the sample is recovered. This is accomplished by purging the condensate trap with zero air and collecting the purged gas in the original sample tank.

11.1.2.2 Begin with the sample tank and condensate trap from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO₂ purge position as shown in Figure 25-9. With the sample tank valve closed, attach the sample tank to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample tank. Next, close the vacuum pump valve, open the sample tank valve, and record the tank pressure.

11.1.2.3 Attach the dry ice-cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO₂ concentration of the trap effluent is less than 5 ppm. CO₂ concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10-ml syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer.

11.1.2.4 After the completion of the CO₂ purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1,060 mm Hg absolute pressure with zero air.

11.1.3 Recovery of the Condensate Trap Sample (See Figure 25-10).

11.1.3.1 Attach the ICV to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow-control and vacuum pump valves.

11.1.3.2 Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 cc/min, then switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate as indicated in Figure 25-10. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow-control valve to maintain atmospheric pressure in the system within 10 percent.

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25

11.1.3.3 Remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If, after 5 minutes, the CO₂ concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C (390 °F). Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO₂ concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 cc/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO₂ concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C (390 °F). If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO₂ concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO₂ purge procedure (Section 11.1.2).

11.1.3.4 After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

11.2 Analysis. Once the initial performance test of the NMO analyzer has been successfully completed (see section 10.1.2) and the daily CO₂ and NMO response factors have been determined (see section 10.2), proceed with sample analysis as follows:

11.2.1 Operating Conditions. The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O₂. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH₄, CO₂, and NMO.

11.2.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO₂ in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO₂ peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (380 °F) as rapidly as possible. A rate of 30 °C/min (90 °F) has been shown to be adequate. Record the value obtained for the condensable organic material (C_{cm}) measured as CO₂ and any measured NMO. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm}.

11.2.3 Analysis of Sample Tank. Perform the analysis as described in section 11.2.2, but record only the value measured for NMO (C_{im}).

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations. All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

12.1 Nomenclature

C = TGNMO 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 ICV, ppm CO₂.

C_t = Calculated noncondensable organic concentration (sample tank) of the effluent, ppm C equivalent.

C_{im} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.

F = Sampling flow rate, cc/min.

L = Volume of liquid injected, μ l.

M = Molecular weight of the liquid injected, g/g-mole.

M_c = TGNMO mass concentration of the effluent, mg C/dsm³.

N = Carbon number of the liquid compound injected (N = 12 for decane, N = 6 for hexane).

n = Number of data points.

P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.

P_b = Barometric pressure, cm Hg.

P_s = Gas sample tank pressure before sampling, mm Hg absolute.

P_a = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.

P_{ff} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

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).

r = Density of liquid injected, g/cc.

T_f = Final temperature of intermediate collection vessel, °K.

T_{if} = Sample tank temperature before sampling, °K.

T_{if} = Sample tank temperature at completion of sampling, °K.

T_{ff} = Sample tank temperature after pressurizing, °K.

V = Sample tank volume, m³.

V_t = Sample train volume, cc.

V_v = Intermediate collection vessel volume, m³.

V_s = Gas volume sampled, dsm³.

x = Individual measurements.

\bar{x} = Mean value.

Pt. 60, App. A-7, Meth. 25

ΔP = Allowable pressure change, cm Hg.
 Θ = Leak-check period, min.

12.2 Allowable Pressure Change. For the pretest leak-check, calculate the allowable pressure change using Equation 25-1:

$$\Delta P = 0.01 \frac{FP_b \Theta}{V_t} \quad \text{Eq. 25-1}$$

12.3 Sample Volume. For each test run, calculate the gas volume sampled using Equation 25-2:

$$V_s = 0.3857 V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right) \quad \text{Eq. 25-2}$$

$$C_c = 0.3857 \frac{V_v P_f}{V_s T_f} \left(\frac{1}{q} \sum_{k=1}^q C_{cm_k} \right) \quad \text{Eq. 25-4}$$

12.6 TGNMO Mass Concentration. Determine the TGNMO mass concentration as carbon for each test run, using Equation 25-5:

$$M_c = 0.4993 (C_t + C_c) \quad \text{Eq. 25-5}$$

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the

condensate recovery and conditioning system using Equation 25-6:

$$\text{Percent Recovery} = K \frac{M V_v P_t C_{cm}}{L P T_f N} \quad \text{Eq. 25-6}$$

where $K = 1.604 \frac{(^{\circ}\text{K})(\text{g-mole})(\%)}{(\text{mm Hg})(\text{mL})(\text{m}^3)(\text{ppm})}$.

12.8 Relative Standard Deviation. Use Equation 25-7 to calculate the relative standard deviation (RSD) of percent recovery and analyzer linearity.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad \text{Eq. 25-7}$$

40 CFR Ch. I (7-1-17 Edition)

12.4 Noncondensable Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C) using Equation 25-3:

$$C_t = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right) \left(\frac{1}{r} \sum_{j=1}^r C_{tm_j} \right) \quad \text{Eq. 25-3}$$

12.5 Condensable Organics. For each condensate trap determine the concentration of organics (ppm C) using Equation 25-4:

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 50 parts per million by volume (ppm). No upper limit has been established.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, A.E., S. Witz, and R.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.

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25

2. Salo, A.E., W.L. Oaks, and R.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.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

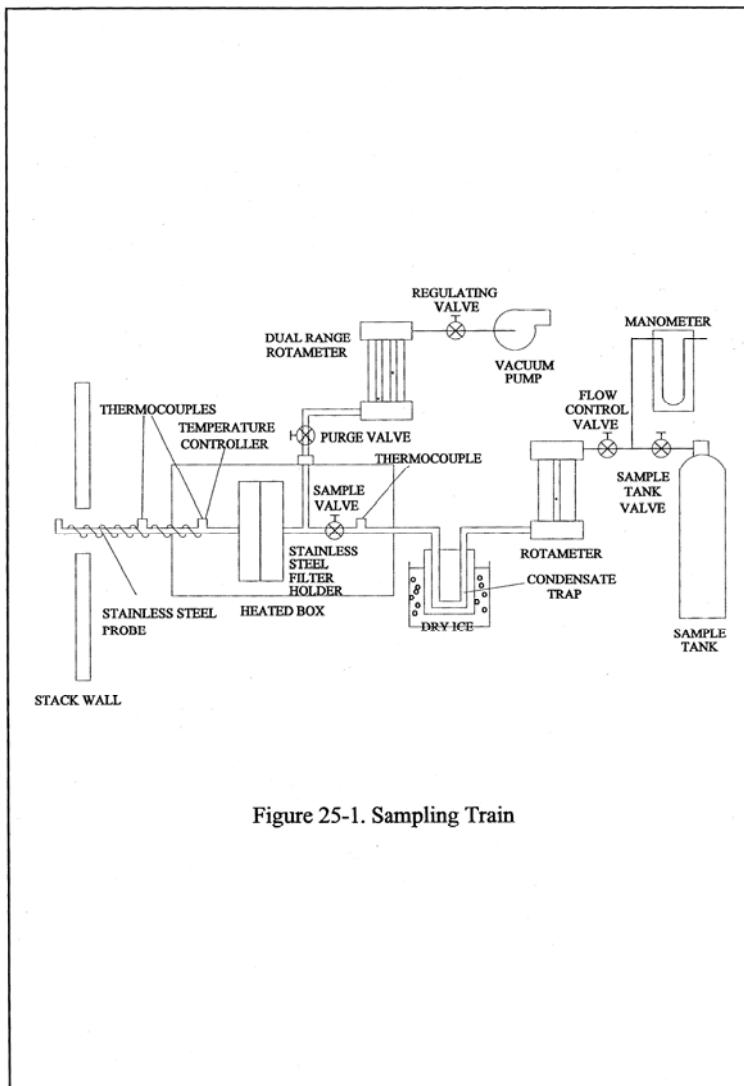


Figure 25-1. Sampling Train

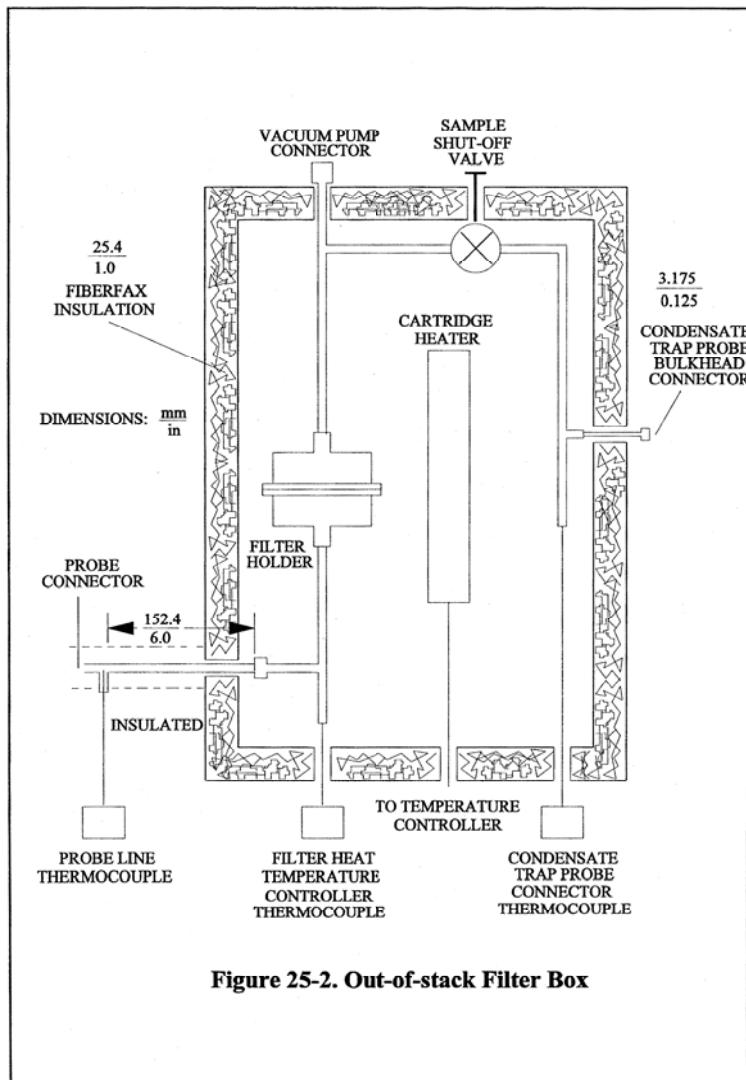


Figure 25-2. Out-of-stack Filter Box

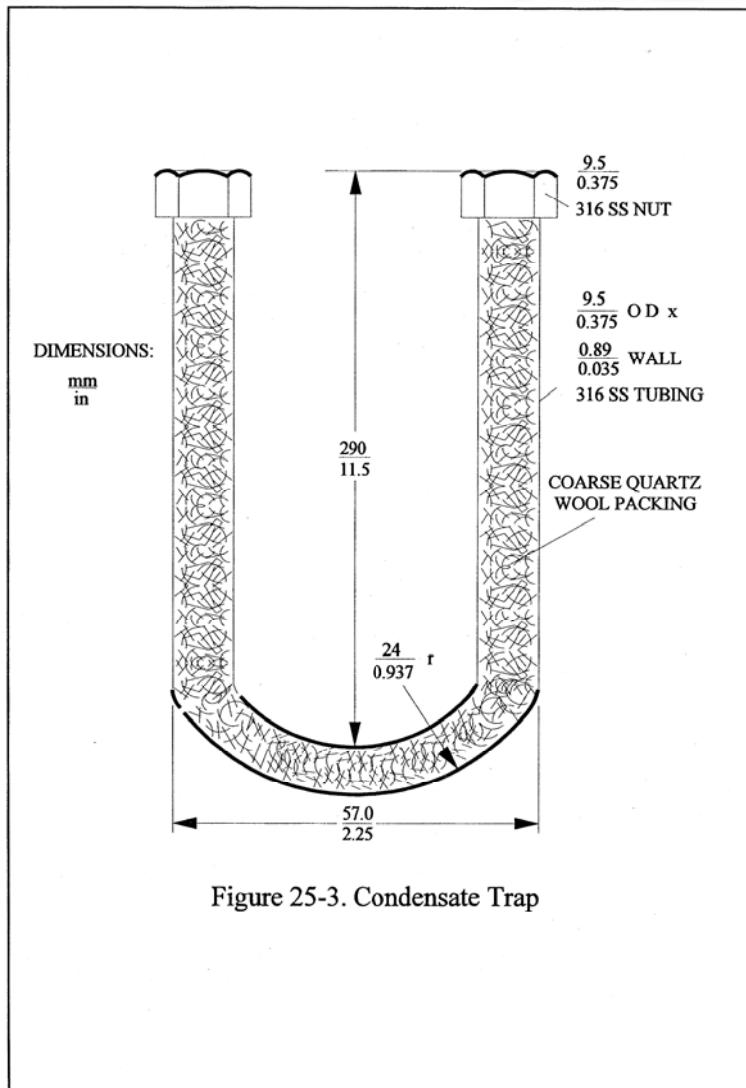
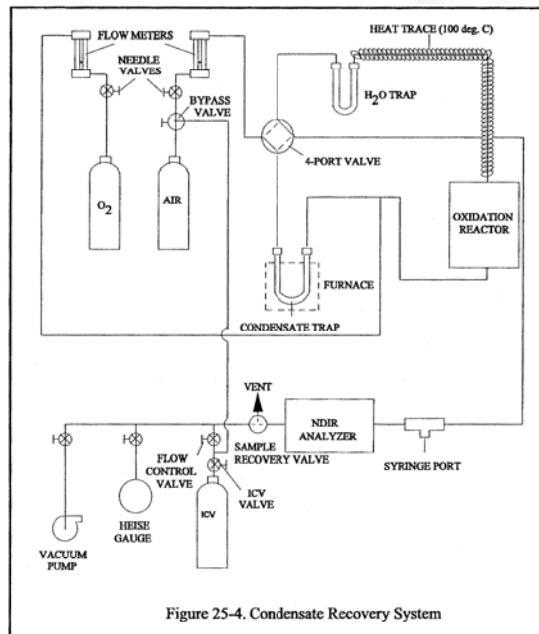


Figure 25-3. Condensate Trap



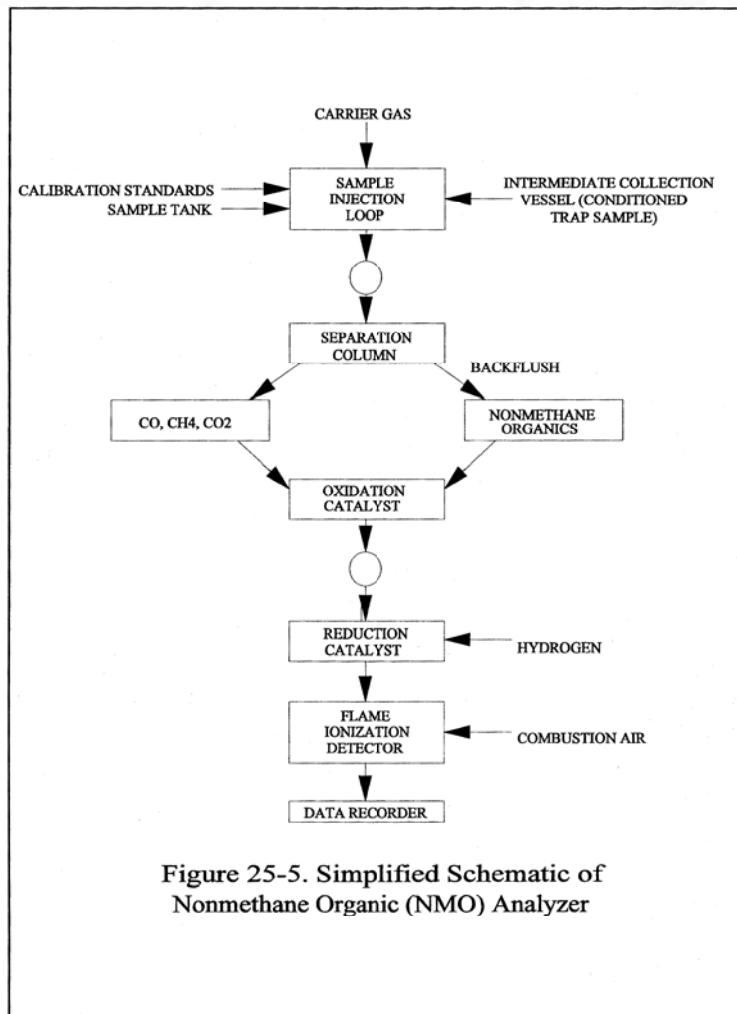
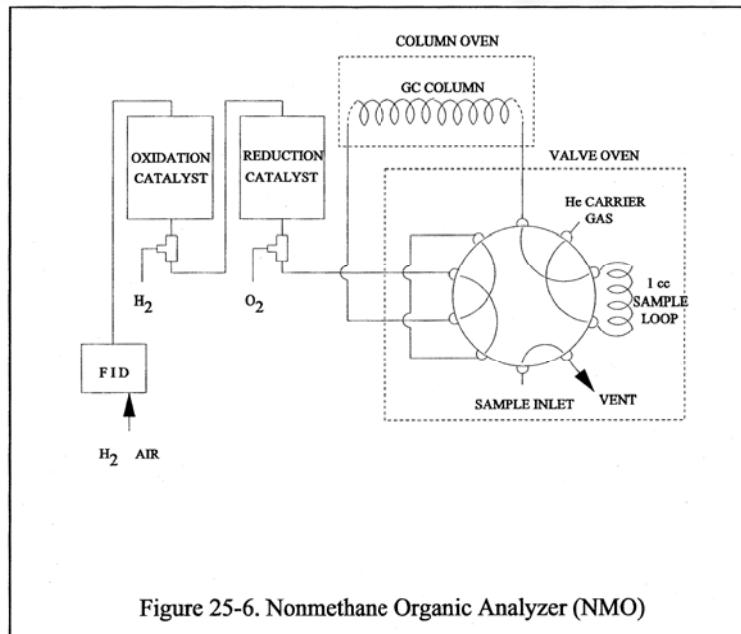


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer



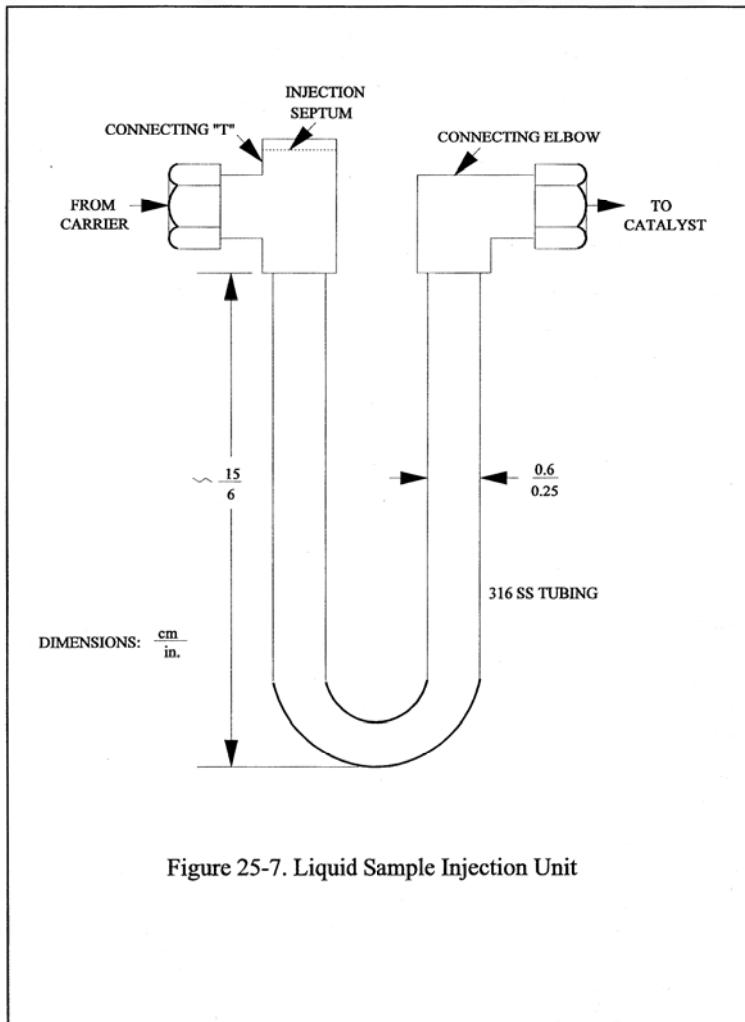
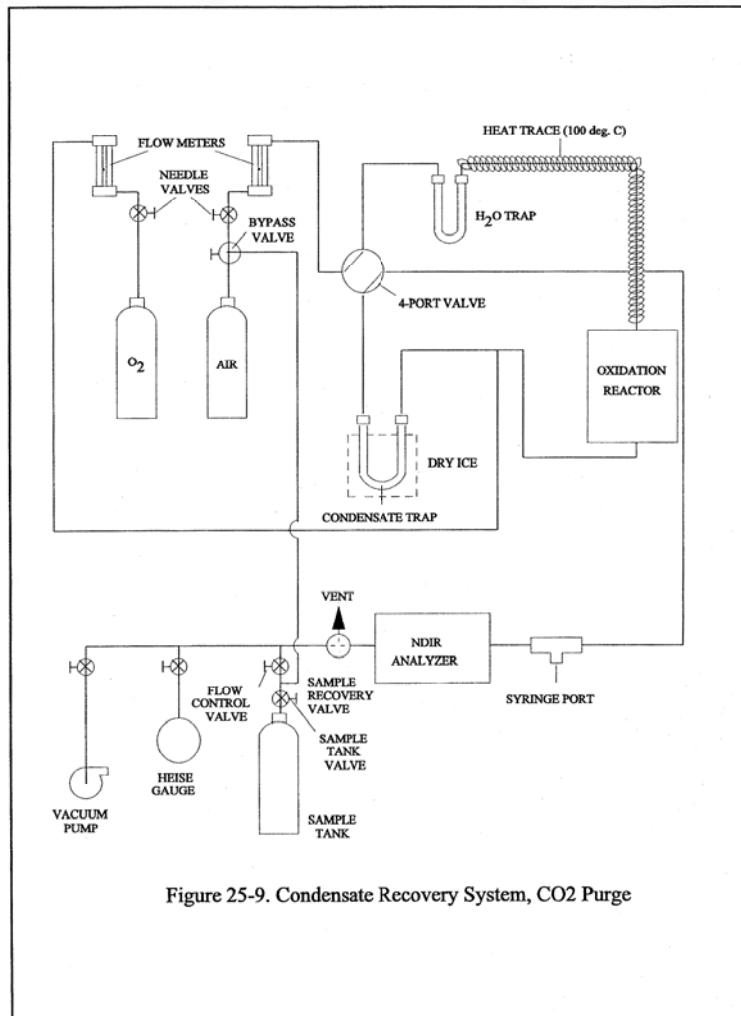


Figure 25-7. Liquid Sample Injection Unit

Figure 25-8. Example Field Data Form

Figure 25-9. Condensate Recovery System, CO₂ Purge

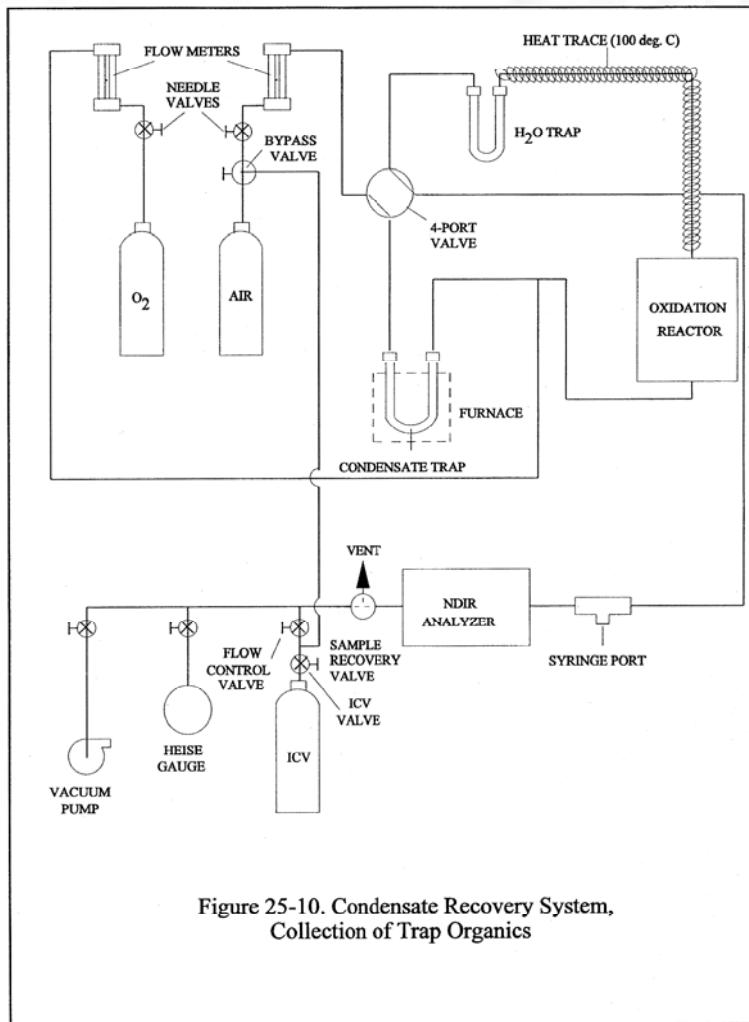


Figure 25-10. Condensate Recovery System,
Collection of Trap Organics

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

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination 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.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line 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.

3.0 Definitions

3.1 Calibration drift means 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.

3.2 Calibration error means the difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3.3 Calibration gas means a known concentration of a gas in an appropriate diluent gas.

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

3.4.1 Sample interface means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 Organic analyzer means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 Response time means 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.

3.6 Span Value means 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.

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

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A-1. All sampling components leading to the analyzer shall be heated $\geq 110^{\circ}\text{C}$ (220°F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated $>120^{\circ}\text{C}$ (250°F).

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) 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.

6.1.3 Heated Sample Line. Stainless steel or Teflon® tubing to transport the sample gas

Pt. 60, App. A-7, Meth. 25A

to the analyzer. The sample line should be heated ($\geq 110^{\circ}\text{C}$) to prevent any condensation.

6.1.4 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.

6.1.5 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.

6.1.6 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.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. 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 (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H₂/60 percent N₂ gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part 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.

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

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

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

40 CFR Ch. I (7-1-17 Edition)**8.0 Sample Collection, Preservation, Storage, and Transport**

8.1 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 to meet the testing requirements of Method 1.

8.2 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.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 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 response. 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 8.6.2). 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.

8.5 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.

8.6 Emission Measurement Test Procedure

8.6.1 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.

Environmental Protection Agency**Pt. 60, App. A-7, Meth. 25A**

8.6.2 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 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 8.4 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).

NOTE: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method section	Quality control measure	Effect
8.4	Zero and calibration drift tests	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic 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.

= 4 for butane.

= Appropriate response factor for other organic calibration gases.

13.0 Method Performance**13.1 Measurement System Performance Specifications.**

13.1.1 Zero Drift. Less than ± 3 percent of the span value.

13.1.2 Calibration Drift. Less than ± 3 percent of span value.

13.1.3 Calibration Error. Less than ± 5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]**15.0 Waste Management [Reserved]****16.0 References**

1. Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency. Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75-GAS-6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data**12.0 Calculations and Data Analysis**

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by 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.

$$C_c = K C_{\text{meas}} \quad \text{Eq. 25A-1}$$

Where:

C_c = Organic concentration as carbon, ppmv.
 C_{meas} = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.

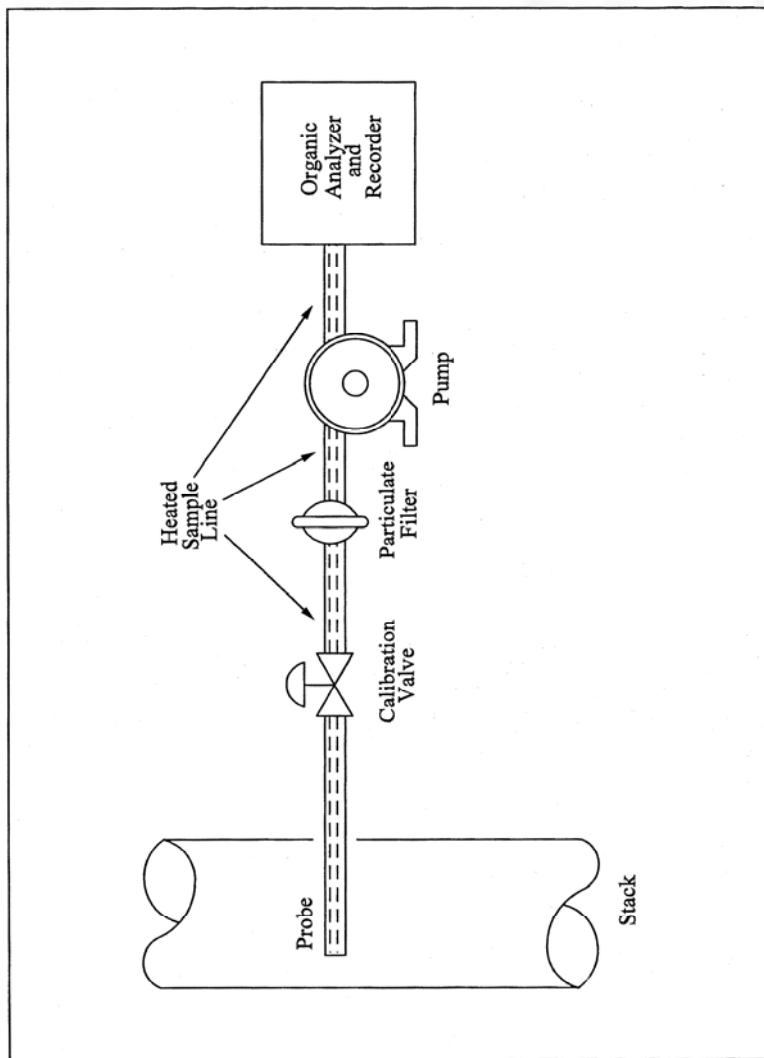


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NON-DISPERSIVE INFRARED ANALYZER

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material is incorporated by reference from other methods

in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 6C, and Method 25A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	<2% of span.

1.2 Applicability. This method is applicable for the determination 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.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

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.

3.0 Definitions

Same as Method 25A, section 3.0.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

Same as Method 25A, section 6.0, with the exception of the following:

6.1 Organic Concentration Analyzer. A non-dispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

7.0 Reagents and Standards

Same as Method 25A, section 7.1. No fuel gas is required for an NDIR.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 25A, section 8.0.

9.0 Quality Control

Same as Method 25A, section 9.0.

10.0 Calibration and Standardization

Same as Method 25A, section 10.0.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Calculations and Data Analysis

Same as Method 25A, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as Method 25A, section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 25C—DETERMINATION OF NONMETHANE ORGANIC COMPOUNDS (NMOC) IN LANDFILL GASES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should also have a thorough knowledge of EPA Method 25.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Nonmethane organic compounds (NMOC).	No CAS number assigned.

1.2 Applicability. This method is applicable to the sampling and measurement of NMOC as carbon in landfill gases (LFG).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 A sample probe that has been perforated at one end is driven or augured to a depth of 0.9 m (3 ft) below the bottom of the landfill cover. A sample of the landfill gas is extracted with an evacuated cylinder. The NMOC content of the gas is determined by

Pt. 60, App. A-7, Meth. 25C

injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO₂), and methane (CH₄); the NMOC are oxidized to CO₂, reduced to CH₄, and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]**4.0 Interferences [Reserved]****5.0 Safety**

5.1 Since this method is complex, only experienced personnel should perform this test. LFG contains methane, therefore explosive mixtures may exist on or near the landfill. It is advisable to take appropriate safety precautions when testing landfills, such as refraining from smoking and installing explosion-proof equipment.

6.0 Equipment and Supplies

6.1 Sample Probe. Stainless steel, with the bottom third perforated. Teflon probe liners and sampling lines are also allowed. Non-perforated probes are allowed as long as they are withdrawn to create a gap equivalent to having the bottom third perforated. The sample probe must be capped at the bottom and must have a threaded cap with a sampling attachment at the top. The sample probe must be long enough to go through and extend no less than 0.9 m (3 ft) below the landfill cover. If the sample probe is to be driven into the landfill, the bottom cap should be designed to facilitate driving the probe into the landfill.

6.2 Sampling Train.

6.2.1 Rotameter with Flow Control Valve. Capable of measuring a sample flow rate of 100 ±10 ml/min. The control valve must be made of stainless steel.

6.2.2 Sampling Valve. Stainless steel.

6.2.3 Pressure Gauge. U-tube mercury manometer, or equivalent, capable of measuring pressure to within 1 mm Hg (0.5 in H₂O) in the range of 0 to 1,100 mm Hg (0 to 590 in H₂O).

6.2.4 Sample Tank. Stainless steel or aluminum cylinder, equipped with a stainless steel sample tank valve.

6.3 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg (5.4 in H₂O).

6.4 Purging Pump. Portable, explosion proof, and suitable for sampling NMOC.

6.5 Pilot Probe Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.1.

6.5.1 Pilot Probe. Tubing of sufficient strength to withstand being driven into the landfill by a post driver and an outside diameter of at least 6 mm (0.25 in.) smaller than the sample probe. The pilot probe shall

40 CFR Ch. I (7-1-17 Edition)

be capped on both ends and long enough to go through the landfill cover and extend no less than 0.9 m (3 ft) into the landfill.

6.5.2 Post Driver and Compressor. Capable of driving the pilot probe and the sampling probe into the landfill. The Kitty Hawk portable post driver has been found to be acceptable.

6.6 Auger Procedure. The following are needed only if the tester chooses to use the procedure described in section 8.2.2.

6.6.1 Auger. Capable of drilling through the landfill cover and to a depth of no less than 0.9 m (3 ft) into the landfill.

6.6.2 Pea Gravel.**6.6.3 Bentonite.**

6.7 NMOC Analyzer, Barometer, Thermometer, and Syringes. Same as in sections 6.3.1, 6.3.2, 6.33, and 6.2.10, respectively, of Method 25.

7.0 Reagents and Standards

7.1 NMOC Analysis. Same as in Method 25, section 7.2.

7.2 Calibration. Same as in Method 25, section 7.4, except omit section 7.4.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Tank Evacuation and Leak-Check. Conduct the sample tank evacuation and leak-check either in the laboratory or the field. Connect the pressure gauge and sampling valve to the sample tank. Evacuate the sample tank to 10 mm Hg (5.4 in H₂O) absolute pressure or less. Close the sampling valve, and allow the tank to sit for 30 minutes. The tank is acceptable if no change more than ±2 mm is noted. Include the results of the leak-check in the test report.

8.2 Sample Probe Installation. The tester may use the procedure in section 8.2.1 or 8.2.2.

8.2.1 Pilot Probe Procedure. Use the post driver to drive the pilot probe at least 0.9 m (3 ft) below the landfill cover. Alternative procedures to drive the probe into the landfill may be used subject to the approval of the Administrator's designated representative.

8.2.1.1 Remove the pilot probe and drive the sample probe into the hole left by the pilot probe. The sample probe shall extend at least 0.9 m (3 ft) below the landfill cover and shall protrude about 0.3 m (1 ft) above the landfill cover. Seal around the sampling probe with bentonite and cap the sampling probe with the sampling probe cap.

8.2.2 Auger Procedure. Use an auger to drill a hole to at least 0.9 m (3 ft) below the landfill cover. Place the sample probe in the hole and backfill with pea gravel to a level 0.6 m (2 ft) from the surface. The sample probe shall protrude at least 0.3 m (1 ft) above the landfill cover. Seal the remaining area around the probe with bentonite. Allow 24

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25C

hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.3 Driven Probes. Closed-point probes may be driven directly into the landfill in a single step. This method may not require backfilling if the probe is adequately sealed by its insertion. Unperforated probes that are inserted in this manner and withdrawn at a distance from a detachable tip to create an open space are also acceptable.

8.3 Sample Train Assembly. Just before assembling the sample train, measure the sample tank vacuum using the pressure gauge. Record the vacuum, the ambient temperature, and the barometric pressure at this time. Assemble the sampling probe purging system as shown in Figure 25C-1.

8.4 Sampling Procedure. Open the sampling valve and use the purge pump and the flow control valve to evacuate at least two sample probe volumes from the system at a flow rate of 500 ml/min or less. Close the sampling valve and replace the purge pump with the sample tank apparatus as shown in Figure 25C-2. Open the sampling valve and the sample tank valve and, using the flow control valve, sample at a flow rate of 500 ml/min or less until either a constant flow rate can no longer be maintained because of reduced sample tank vacuum or the appropriate composite volume is attained. Disconnect the sampling tank apparatus and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H₂O) absolute pressure with he-

lium, and record the final pressure. Alternatively, the sample tank may be pressurized in the lab.

8.4.1 The following restrictions apply to compositing samples from different probe sites into a single cylinder: (1) Individual composite samples per cylinder must be of equal volume; this must be verified by recording the flow rate, sampling time, vacuum readings, or other appropriate volume measuring data, (2) individual composite samples must have a minimum volume of 1 liter unless data is provided showing smaller volumes can be accurately measured, and (3) composite samples must not be collected using the final cylinder vacuum as it diminishes to ambient pressure.

8.4.2 Use Method 3C to determine the percent N₂ in each cylinder. The presence of N₂ indicates either infiltration of ambient air into the landfill gas sample or an inappropriate testing site has been chosen where anaerobic decomposition has not begun. The landfill gas sample is acceptable if the concentration of N₂ is less than 20 percent. Alternatively, Method 3C may be used to determine the oxygen content of each cylinder as an air infiltration test. With this option, the oxygen content of each cylinder must be less than 5 percent.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.4.2	Verify that landfill gas sample contains less than 20 percent N ₂ or 5 percent O ₃ .	Ensures that ambient air was not drawn into the landfill gas sample and gas was sampled from an appropriate location.
10.1, 10.2	NMOC analyzer initial and daily performance checks.	Ensures precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial NMOC Analyzer Performance Test. Same as in Method 25, section 10.1, except omit the linearity checks for CO₂ standards.

10.2 NMOC Analyzer Daily Calibration.

10.2.1 NMOC Response Factors. Same as in Method 25, section 10.2.2.

10.3 Sample Tank Volume. The volume of the gas sampling tanks must be determined. Determine the tank volumes by weighing them empty and then filled with deionized water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 ml.

11.0 Analytical Procedures

11.1 The oxidation, reduction, and measurement of NMOC's is similar to Method 25. Before putting the NMOC analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order. Conduct the performance test according to the procedures established in section 10.1. Once the performance test has been successfully completed and the NMOC calibration response factor has been determined, proceed with sample analysis as follows:

11.1.1 Daily Operations and Calibration Checks. Before and immediately after 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 10.2. If the criteria of the daily calibration test cannot be met, repeat

Pt. 60, App. A-7, Meth. 25C

the NMOC analyzer performance test (Section 10.1) before proceeding.

11.1.2 Operating Conditions. Same as in Method 25, section 11.2.1.

11.1.3 Analysis of Sample Tank. Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO₂ in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO₂ peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 °C (383 °F) as rapidly as possible. A rate of 30 °C/min (54 °F/min) has been shown to be adequate. Record the value obtained for any measured NMOC. Return the column oven temperature to 85 °C (185 °F) in preparation for the next analysis. Analyze each sample in triplicate, and report the average as C_m.

12.0 Data Analysis and Calculations

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

12.1 Nomenclature

B_w = Moisture content in the sample, fraction.

C_{N2} = N₂ concentration in the diluted sample gas.

C_{mN2} = Measured N₂ concentration, fraction in landfill gas.

C_{mox} = Measured Oxygen concentration, fraction in landfill gas.

40 CFR Ch. I (7-1-17 Edition)

C_{Ox} = Oxygen concentration in the diluted sample gas.

C_i = Calculated NMOC concentration, ppmv C equivalent.

C_m = Measured NMOC concentration, ppmv C equivalent.

P_b = Barometric pressure, mm Hg.

P_t = Gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

P_{te} = Gas sample tank pressure after evacuation, mm Hg absolute.

P_w = Vapor pressure of H₂O (from Table 25C-1), mm Hg.

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).

T_t = Sample tank temperature at completion of sampling, °K.

T_{te} = Sample tank temperature before sampling, °K.

T_{tf} = Sample tank temperature after pressuring, °K.

12.2 Water Correction. Use Table 25C-1 (Section 17.0), the LFG temperature, and barometric pressure at the sampling site to calculate B_w.

$$B_w = \frac{P_w}{P_b} \quad \text{Eq. 25C-1}$$

12.3 Nitrogen Concentration in the landfill gas. Use equation 25C-2 to calculate the measured concentration of nitrogen in the original landfill gas.

$$C_{N2} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}} \right)}{\left(\left(\frac{P_t}{T_t} \right) - \left(\frac{P_{ti}}{T_{ti}} \right) \right)} \right] C_{mN2} \quad \text{Eq. 25C-2}$$

12.4 Oxygen Concentration in the landfill gas. Use equation 25C-3 to calculate the

measured concentration of oxygen in the original landfill gas.

$$C_{Ox} = \left[\frac{\left(\frac{P_{tf}}{T_{tf}} \right)}{\left(\left(\frac{P_t}{T_t} \right) - \left(\frac{P_{ti}}{T_{ti}} \right) \right)} \right] C_{mox} \quad \text{Eq. 25C-3}$$

12.5 You must correct the NMOC Concentration for the concentration of nitrogen

or oxygen based on which gas or gases passes the requirements in section 9.1.

12.5.1 NMOC Concentration with nitrogen correction. Use Equation 25C-4 to calculate the concentration of NMOC for each sample

tank when the nitrogen concentration is less than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t - P_{ti}}{T_t - T_{ti}}\right)\left(1 - \frac{99}{78}C_{N2}\right) - B_w} \frac{1}{r} \sum_{j=1}^r C_{tm(j)} \quad \text{Eq. 25C-4}$$

12.5.2 NMOC Concentration with oxygen correction. Use Equation 25C-5 to calculate the concentration of NMOC for each sample

tank if the landfill gas oxygen is less than 5 percent and the landfill gas nitrogen concentration is greater than 20 percent.

$$C_t = \frac{\frac{P_{tf}}{T_{tf}}}{\left(\frac{P_t - P_{ti}}{T_t - T_{ti}}\right)\left(1 - \frac{99}{21}C_{Ox}\right) - B_w} \frac{1}{r} \sum_{j=1}^r C_{tm(j)} \quad \text{Eq. 25C-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

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, Massachusetts. June 15-20, 1975.) 14 p.

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, Colorado. June 9-13, 1974.) 25 p.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

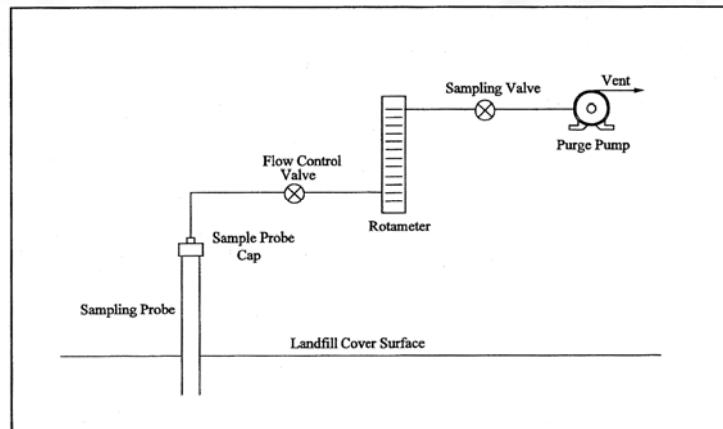


Figure 25C-1. Schematic of Sampling Probe Purging System

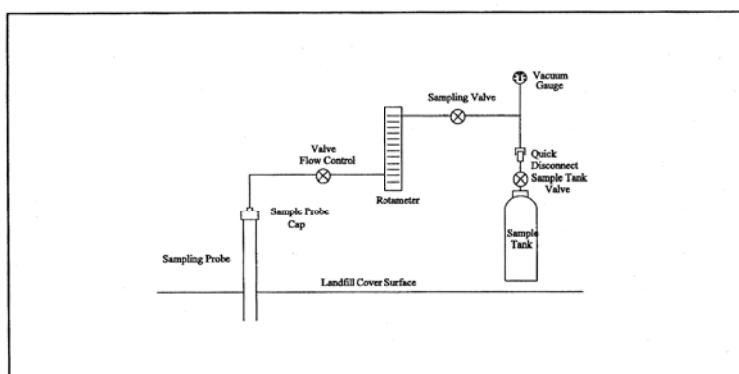


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C-1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H ₂ O, mm Hg	Tempera-ture, °C	Vapor Pressure of H ₂ O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3

TABLE 25C-1—MOISTURE CORRECTION—Continued

Temperature, °C	Vapor Pressure of H ₂ O, mm Hg	Tempera-ture, °C	Vapor Pressure of H ₂ O, mm Hg
16	13.6	30	31.8

Environmental Protection Agency

METHOD 25D—DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or an electrolytic conductivity detector (ELCD) because knowledge beyond the scope of this presentation is required.

1.0 Scope and Application

1.1 Analyte. Volatile Organic Compounds. No CAS No. assigned.

1.2 Applicability. This method is applicable for determining the volatile organic (VO) concentration of a waste sample.

2.0 Summary of Method

2.1 Principle. A sample of waste is obtained at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). The sample is suspended in an organic/aqueous matrix, then heated and purged with nitrogen for 30 min. in order to separate certain organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an ELCD. The VO concentration is the sum of the carbon and chlorine content of the sample.

3.0 Definitions

3.1 *Well-mixed* in the context of this method refers to turbulent flow which results in multiple-phase waste in effect behaving as single-phase waste due to good mixing.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

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

6.1 Sampling. The following equipment is required:

6.1.1 Sampling Tube. Flexible Teflon, 0.25 in. ID (6.35 mm).

6.1.2 Sample Container. Borosilicate glass, 40-mL, and a Teflon-lined screw cap capable of forming an air tight seal.

Pt. 60, App. A-7, Meth. 25D

6.1.3 Cooling Coil. Fabricated from 0.25 in (6.35 mm), ID 304 stainless steel tubing with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Purging Apparatus. For separating the VO from the waste sample. A schematic of the system is shown in Figure 25D-1. The purging apparatus consists of the following major components.

6.2.1.1 Purging Flask. A glass container to hold the sample while it is heated and purged with dry nitrogen. The cap of the purging flask is equipped with three fittings: one for a purging lance (fitting with the #7 Ace-thread), one for the Teflon exit tubing (side fitting, also a #7 Ace-thread), and a third (a 50-mm Ace-thread) to attach the base of the purging flask as shown in Figure 25D-2. The base of the purging flask is a 50-mm ID (2 in) cylindrical glass tube. One end of the tube is open while the other end is sealed. Exact dimensions are shown in Figure 25D-2.

6.2.1.2 Purging Lance. Glass tube, 6-mm OD (0.2 in) by 30 cm (12 in) long. The purging end of the tube is fitted with a four-arm bubbler with each tip drawn to an opening 1 mm (0.04 in) in diameter. Details and exact dimensions are shown in Figure 25D-2.

6.2.1.3 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging flask. The details of the design are shown in Figure 25D-3.

6.2.1.4 Constant Temperature Chamber. A forced draft oven capable of maintaining a uniform temperature around the purging flask and coalescing filter of $75 \pm 2^\circ\text{C}$ ($167 \pm 3.6^\circ\text{F}$).

6.2.1.5 Three-way Valve. Manually operated, stainless steel. To introduce calibration gas into system.

6.2.1.6 Flow Controllers. Two, adjustable. One capable of maintaining a purge gas flow rate of $6 \pm 0.06 \text{ L/min}$ ($0.2 \pm 0.002 \text{ ft}^3/\text{min}$). The other capable of maintaining a calibration gas flow rate of $1\text{--}100 \text{ mL/min}$ ($0.00004\text{--}0.004 \text{ ft}^3/\text{min}$).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft³/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to $120 \pm 10^\circ\text{C}$ ($248 \pm 18^\circ\text{F}$)). At a purge rate of 6 L/min (0.2 ft³/min), one will supply a constant flow to the first detector (the rest of the flow will be directed to the second sample splitter). The second splitter will split the analytical flow between the second detector and the flow restrictor. The approximate flow to the FID will be 40 mL/min (0.0014 ft³/min) and to the ELCD will be 15 mL/min (0.0005 ft³/min), but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement. The two sample splitters will be connected to each other by 1/8" OD (3.175 mm) stainless steel tubing.

Pt. 60, App. A-7, Meth. 25D**40 CFR Ch. I (7-1-17 Edition)**

6.2.1.9 Flow Restrictor. Stainless steel tubing, 1/8' OD (3.175 mm), connecting the second sample splitter to the ice bath. Length is determined by the resulting pressure in the purging flask (as measured by the pressure gauge). The resulting pressure from the use of the flow restrictor shall be 6-7 psig.

6.2.1.10 Filter Flask. With one-hole stopper. Used to hold ice bath. Excess purge gas is vented through the flask to prevent condensation in the flowmeter and to trap volatile organic compounds.

6.2.1.11 Four-way Valve. Manually operated, stainless steel. Placed inside oven, used to bypass purging flask.

6.2.1.12 On/Off Valves. Two, stainless steel. One heat resistant up to 130 °C (266 °F) and placed between oven and ELCD. The other a toggle valve used to control purge gas flow.

6.2.1.13 Pressure Gauge. Range 0-40 psi. To monitor pressure in purging flask and coalescing filter.

6.2.1.14 Sample Lines. Teflon, 1/4' OD (6.35 mm), used inside the oven to carry purge gas to and from purging chamber and to and from coalescing filter to four-way valve. Also used to carry sample from four-way valve to first sample splitter.

6.2.1.15 Detector Tubing. Stainless steel, 1/8' OD (3.175 mm), heated to 120 ±10 °C (248 ±18 °F). Used to carry sample gas from each sample splitter to a detector. Each piece of tubing must be wrapped with heat tape and insulating tape in order to insure that no cold spots exist. The tubing leading to the ELCD will also contain a heat-resistant on/off valve (Section 6.2.1.12) which shall also be wrapped with heat-tape and insulation.

6.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample and an ELCD to measure the chlorine concentration.

6.2.2.1 FID. A heated FID meeting the following specifications is required.

6.2.2.1.1 Linearity. A linear response (± 5 percent) over the operating range as demonstrated by the procedures established in section 10.1.1.

6.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 µg carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.1.3 Data Recording System. A digital integration system compatible with the FID for permanently recording the output of the detector. The recorder shall have the capability to start and stop integration at points selected by the operator or it shall be capable of the "integration by slices" technique (this technique involves breaking down the chromatogram into smaller increments, integrating the area under the curve for each portion, subtracting the background for each portion, and then adding all of the areas together for the final area count).

6.2.2.2 ELCD. An ELCD meeting the following specifications is required. 1-propanol must be used as the electrolyte. The electrolyte flow through the conductivity cell shall be 1 to 2 mL/min (0.00004 to 0.00007 ft³/min).

NOTE: A 1/4-in. ID (6.35 mm) quartz reactor tube is strongly recommended to reduce carbon buildup and the resulting detector maintenance.

6.2.2.2.1 Linearity. A linear response (± 10 percent) over the response range as demonstrated by the procedures in section 10.1.2.

6.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.2.2.2.3 Data Recording System. A digital integration system compatible with the output voltage range of the ELCD. The recorder must have the capability to start and stop integration at points selected by the operator or it shall be capable of performing the "integration by slices" technique.

7.0 Reagents and Standards**7.1 Sampling.**

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure with an average molecular weight of 400. Before using the PEG, remove any organic compounds that might be detected as volatile organics by heating it to 120 °C (248 °F) and purging it with nitrogen at a flow rate of 1 to 2 L/min (0.04 to 0.07 ft³/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft³/min) nitrogen purge until use. The purga apparatus is shown in Figure 25D-4.

7.2 Analysis.

7.2.1 Sample Separation. The following are required for the sample purging step.

7.2.1.1 PEG. Same as section 7.1.1.

7.2.1.2 Purge Gas. Zero grade nitrogen (N₂), containing less than 1 ppm carbon.

7.2.2 Volatile Organics Measurement. The following are required for measuring the VO concentration.

7.2.2.1 Hydrogen (H₂). Zero grade H₂, 99.999 percent pure.

7.2.2.2 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2.2.3 Calibration Gas. Pressurized gas cylinder containing 10 percent propane and 1 percent 1,1-dichloroethylene by volume in nitrogen.

7.2.2.4 Water. Deionized distilled water that conforms to American Society for Testing and Materials Specification D 1193-74, Type 3, is required for analysis. At the option of the analyst, the KMnO₄ test for oxidizable organic matter may be omitted when high concentrations are not expected to be present.

7.2.2.5 1-Propanol. ACS grade or better. Electrolyte Solution. For use in the ELCD.

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25D

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Sampling Plan Design and Development. Use the procedures in chapter nine of Reference 1 in section 16 as guidance in developing a sampling plan.

8.1.2 Single Phase or Well-mixed Waste.

8.1.2.1 Install a sampling tap to obtain the sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to the atmosphere). Assemble the sampling apparatus as shown in Figure 25D-5.

8.1.2.2 Prepare the sampling containers as follows: Pour 30 mL of clean PEG into the container. PEG will reduce but not eliminate the loss of organics during sample collection. Weigh the sample container with the screw cap, the PEG, and any labels to the nearest 0.01 g and record the weight (m_s). Store the containers in an ice bath until 1 hour before sampling (PEG will solidify at ice bath temperatures; allow the containers to reach room temperature before sampling).

8.1.2.3 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.1.2.4 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in section 8.1.2.2. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10 °C (50 °F). Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

8.1.3 Multiple-phase Waste. Collect a 10 g sample of each phase of waste generated using the procedures described in section 8.1.2 or 8.1.5. Each phase of the waste shall be analyzed as a separate sample. Calculate the weighted average VO concentration of the waste using Equation 25D-13 (Section 12.14).

8.1.4 Solid waste. Add approximately 10 g of the solid waste to a container prepared in the manner described in section 8.1.2.2, minimizing headspace. Cap and chill immediately.

8.1.5 Alternative to Tap Installation. If tap installation is impractical or impossible, fill a large, clean, empty container by submerging the container into the waste below the surface of the waste. Immediately fill a container prepared in the manner described in section 8.1.2.2 with approximately 10 g of the waste collected in the large container. Minimize headspace, cap and chill immediately.

8.1.6 Alternative sampling techniques may be used upon the approval of the Administrator.

8.2 Sample Recovery.

8.2.1 Assemble the purging apparatus as shown in Figures 25D-1 and 25D-2. The oven shall be heated to 75 ±2 °C (167 ±3.6 °F). The sampling lines leading from the oven to the detectors shall be heated to 120 ±10 °C (248 ±18 °F) with no cold spots. The flame ionization detector shall be operated with a heated block. Adjust the purging lance so that it reaches the bottom of the chamber.

8.2.2 Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container to the nearest 0.01 g, and record the weight (m_f). Pour the contents of the sample container into the purging flask, rinse the sample container three times with a total of 20 mL of PEG (since the sample container originally held 30 mL of PEG, the total volume of PEG added to the purging flask will be 50 mL), transferring the rinsings to the purging flask after each rinse. Cap purging flask between rinses. The total volume of PEG in the purging flask shall be 50 mL. Add 50 mL of water to the purging flask.

9.0 Quality Control

9.1 Quality Control Samples. If audit samples are not available, prepare and analyze the two types of quality control samples (QCS) listed in Sections 9.1.1 and 9.1.2. Before placing the system in operation, after a shutdown of greater than six months, and after any major modifications, analyze each QCS in triplicate. For each detector, calculate the percent recovery by dividing measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be ≤10 percent. For QCS 1 (methylene chloride), the percent recovery shall be ≥90 percent for carbon as methane, and ≥55 percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be ≤15 percent for carbon as methane, and ≤6 percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55 µL of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 µL of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze

the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 3.777×10^{-3} . To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by 1.670×10^{-2} .

9.1.2 QCS 2. 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60 μ L of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100 μ L of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in sections 10.2 and 10.3, excluding section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 7.461×10^{-3} . To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by 1.099×10^{-2} .

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be ± 13 percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the ± 13 percent criteria.

10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D-1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in section 7.2,2,3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D-3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, (m_c) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D-4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass (m_{ch}) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the

FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D-1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D-5 and 25D-6) and the relative standard deviation (RSD) (Equation 25D-10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2 Daily Calibrations

10.2.1 Daily Linearity Check. Follow the procedures outlined in section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat sections 10.1.1 and 10.1.2.

10.2.2 Calibration Range Check

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in section 10.1.1 to choose two calibration points that bracket the new target

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25D

concentration. Analyze each of these points in triplicate (as outlined in section 10.1.1) and use the criteria in section 10.1.2 to determine the linearity of the detector in this "mini-calibration" range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

11.0 Analysis

11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at $75 \pm 2^\circ\text{C}$ ($167 \pm 3.6^\circ\text{F}$). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches $75 \pm 2^\circ\text{C}$ ($167 \pm 3.6^\circ\text{F}$), start both integrators and record baseline. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D-6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in sections 8.2 and 8.3, excluding section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to ≤ 10 percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

- A_b = Area under the water blank response curve, counts.
 A_c = Area under the calibration response curve, counts.
 A_s = Area under the sample response curve, counts.
 C = Concentration of volatile organics in the sample, ppmw.
 C_c = Concentration of carbon, as methane, in the calibration gas, mg/L.
 C_{ch} = Concentration of chloride in the calibration gas, mg/L.
 C_j = VO concentration of phase j, ppmw.
 DR_i = Average daily response factor of the FID, mg CH₄/counts.
 DR_{ih} = Average daily response factor of the ELCD, mg Cl⁻/counts.
 F_j = Weight fraction of phase j present in the waste.
 m_c = Mass of carbon, as methane, in a calibration run, mg.
 m_{ch} = Mass of chloride in a calibration run, mg.
 m_s = Mass of the waste sample, g.
 m_{sc} = Mass of carbon, as methane, in the sample, mg.
 m_{sf} = Mass of sample container and waste sample, g.
 m_{sh} = Mass of chloride in the sample, mg.
 m_{si} = Mass of sample container prior to sampling, g.
 m_{vo} = Mass of volatile organics in the sample, mg.
 n = Total number of phases present in the waste.
 P_p = Percent propane in calibration gas (L/L).
 P_{ve} = Percent 1,1-dichloroethylene in calibration gas (L/L).
 Q_c = Flow rate of calibration gas, L/min.
 t_e = Length of time standard gas is delivered to the analyzer, min.
 W = Weighted average VO concentration, ppmw.
12.2 Concentration of Carbon, as Methane, in the Calibration Gas.

$$C_c = (19.681 \times P_p) + (13.121 \times P_{vc}) \quad \text{Eq. 25D-1}$$

12.3 Concentration of Chloride in the Calibration Gas.

$$C_{ch} = 28.998 \times P_{vc} \quad \text{Eq. 25D-2}$$

12.4 Mass of Carbon, as Methane, in a Calibration Run.

$$M_c = C_c \times Q_c \times t_c \quad \text{Eq. 25D-3}$$

12.5 Mass of Chloride in a Calibration Run.

$$m_{ch} = C_{ch} \times Q_c \times t_c \quad \text{Eq. 25D-4}$$

12.6 FID Response Factor, mg/counts.

$$DR_t = \frac{m_c}{A_c} \quad \text{Eq. 25D-5}$$

12.7 ELCD Response Factor, mg/counts.

$$DR_{th} = \frac{m_{ch}}{A_c} \quad \text{Eq. 25D-6}$$

12.8 Mass of Carbon in the Sample.

$$m_{sc} = DR_t (A_s - A_b) \quad \text{Eq. 25D-7}$$

12.9 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th} (A_s - A_b) \quad \text{Eq. 25D-8}$$

12.10 Mass of Volatile Organics in the Sample.

$$m_{vo} = m_{sc} + m_{sh} \quad \text{Eq. 25D-9}$$

12.11 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad \text{Eq. 25D-10}$$

12.12 Mass of Sample.

$$m_s = m_{sf} - m_{st} \quad \text{Eq. 25D-11}$$

12.13 Concentration of Volatile Organics in Waste.

$$C = \frac{(m_{vo} \times 1000)}{m_s} \quad \text{Eq. 25D-12}$$

12.14 Weighted Average VO Concentration of Multi-phase Waste.

$$W = \sum_{j=1}^n F_j x \bar{C}_j \quad \text{Eq. 25D-13}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. "Test Methods for Evaluating Solid Waste, Physical/Chemistry Methods", U.S. Environmental Protection Agency, Publication SW-846, 3rd Edition, November 1986 as amended by Update I, November 1990.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

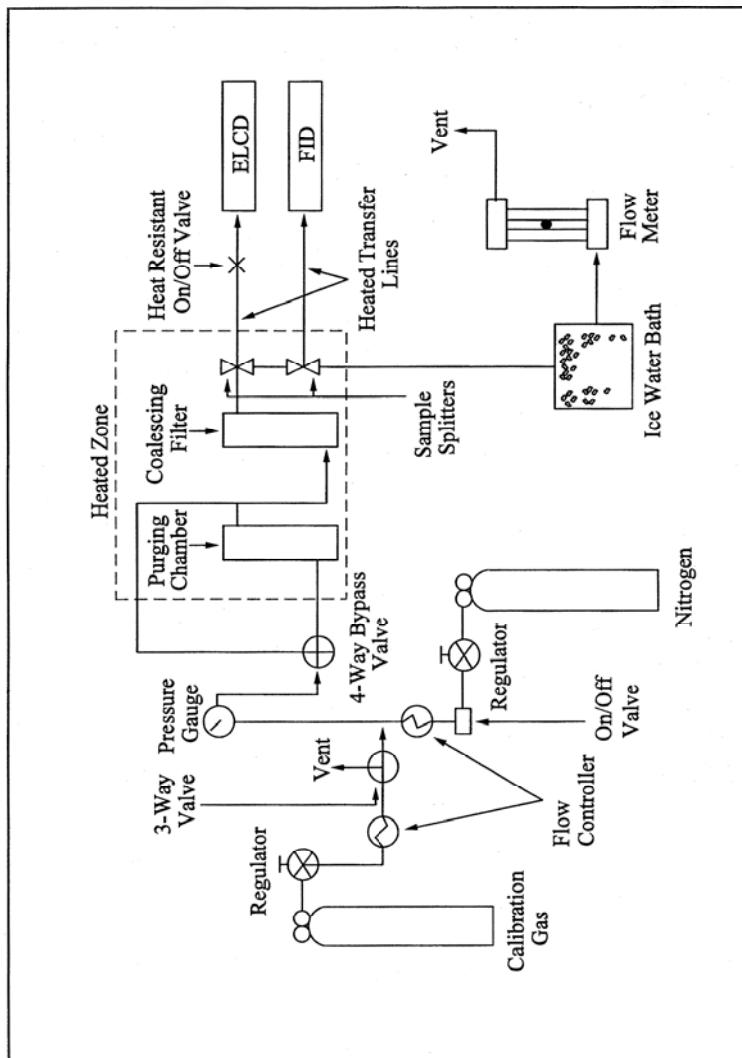


Figure 25D-1. Schematic of Purging Apparatus.

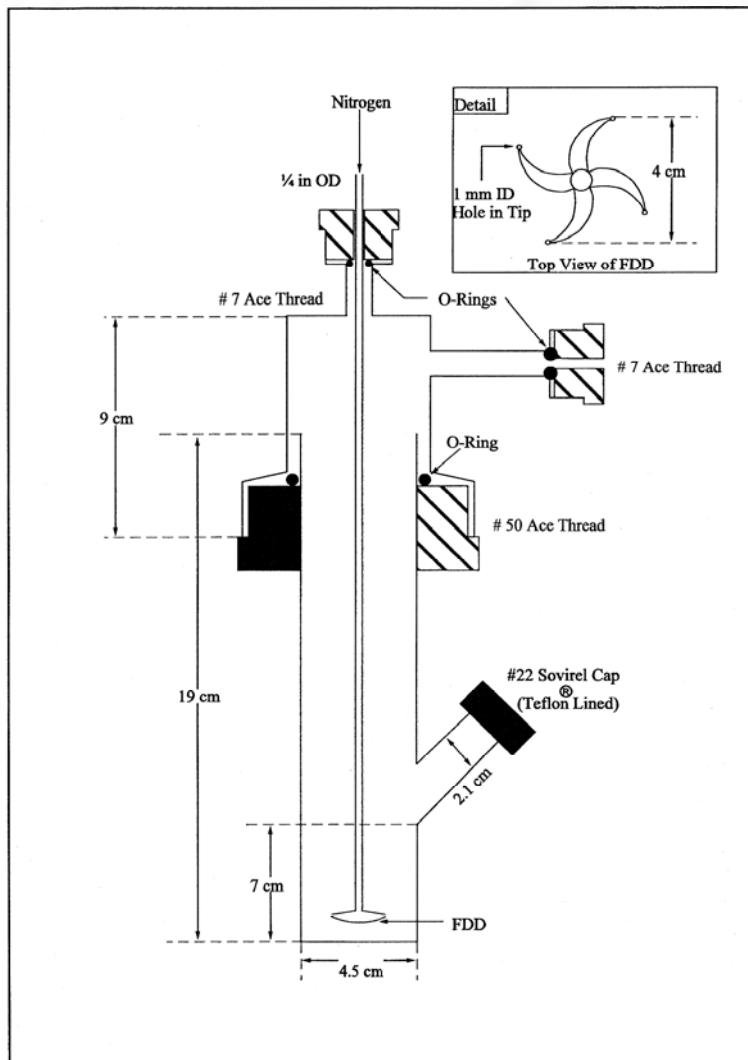
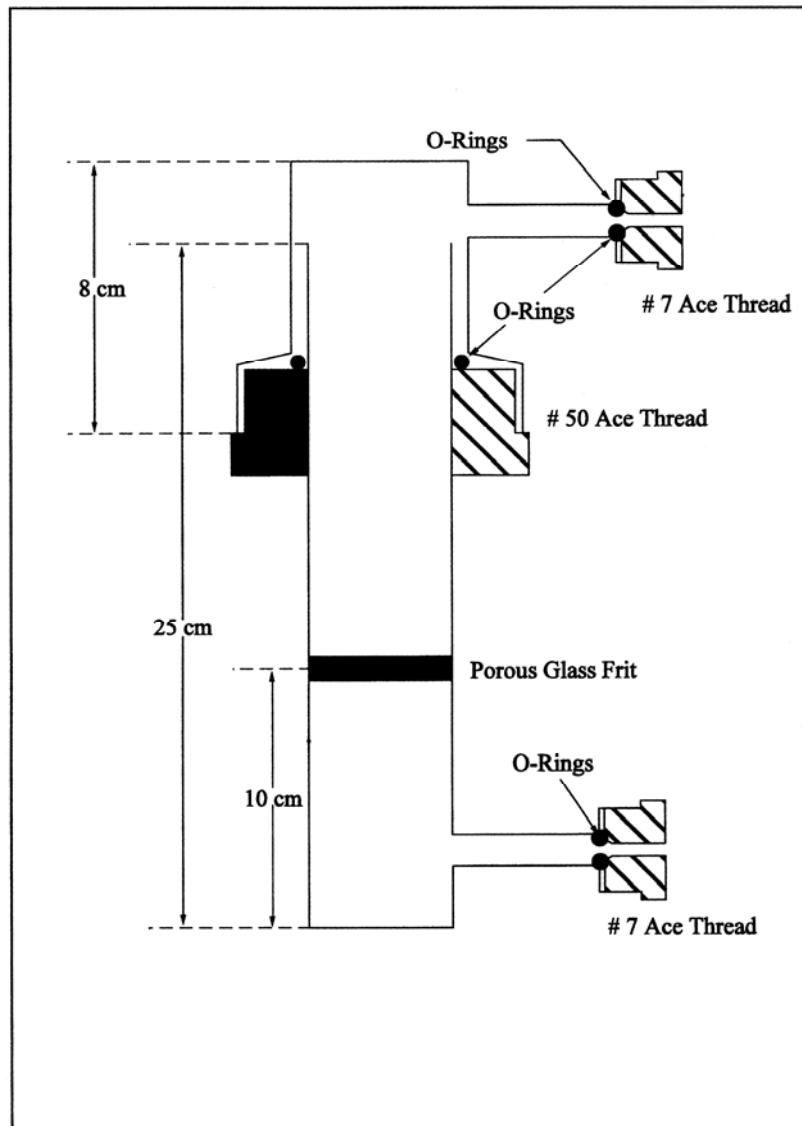


Figure 25D-2. Purging Lance.



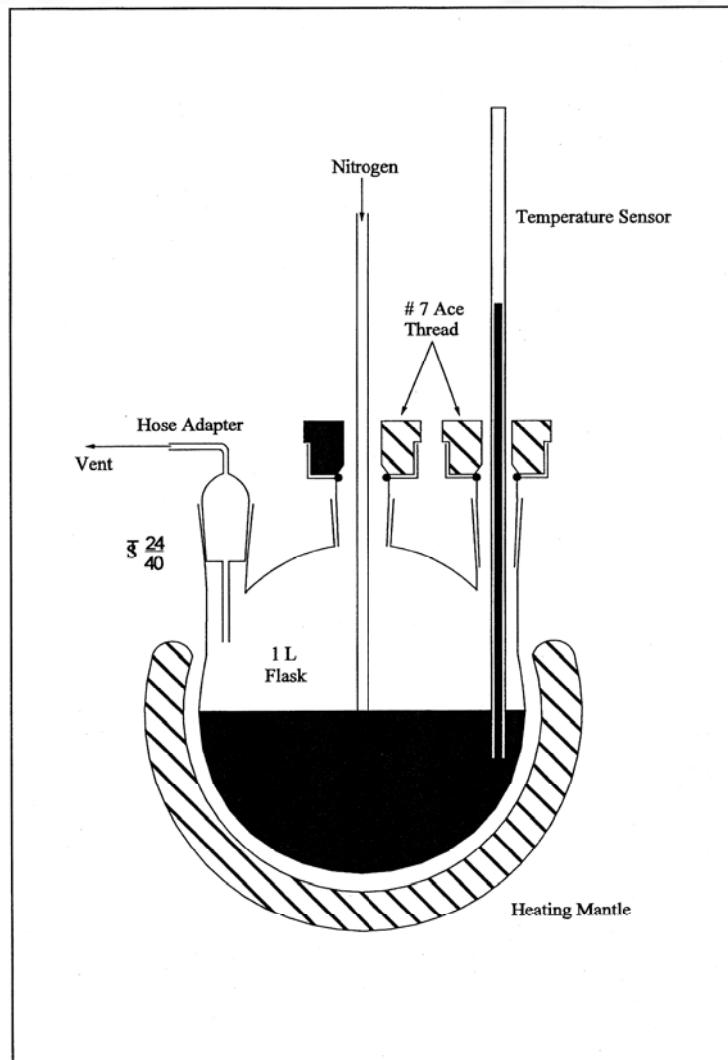


Figure 25D-4. Schematic of PEG Cleaning System.

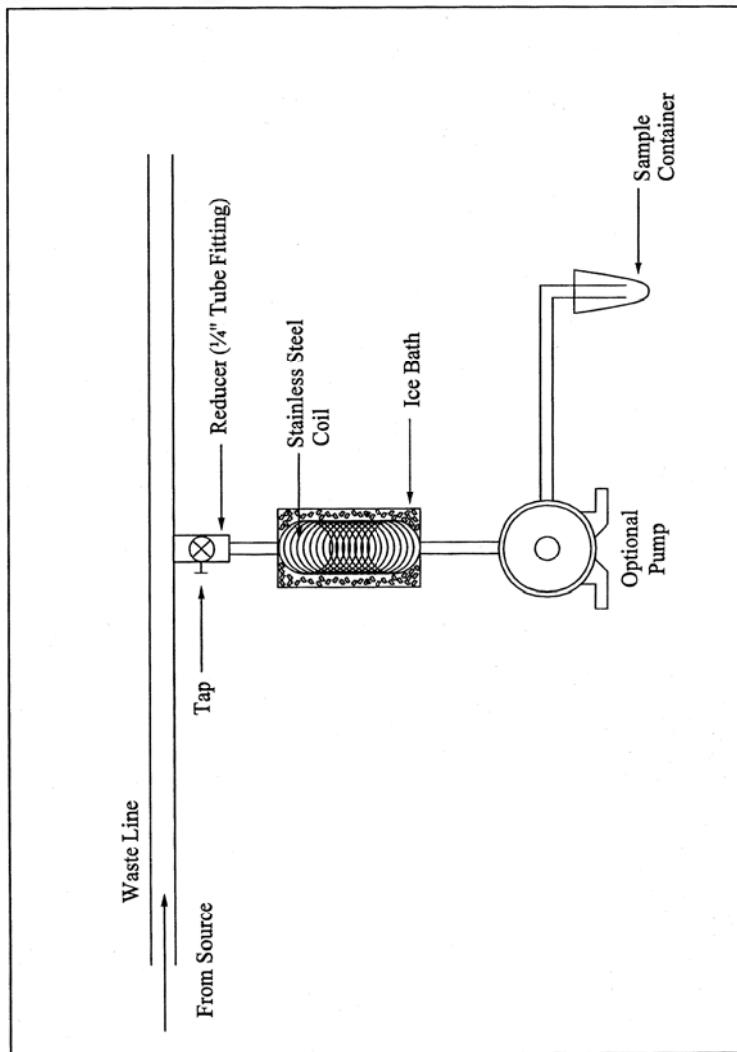


Figure 25D-5. Schematic of Sampling Apparatus.

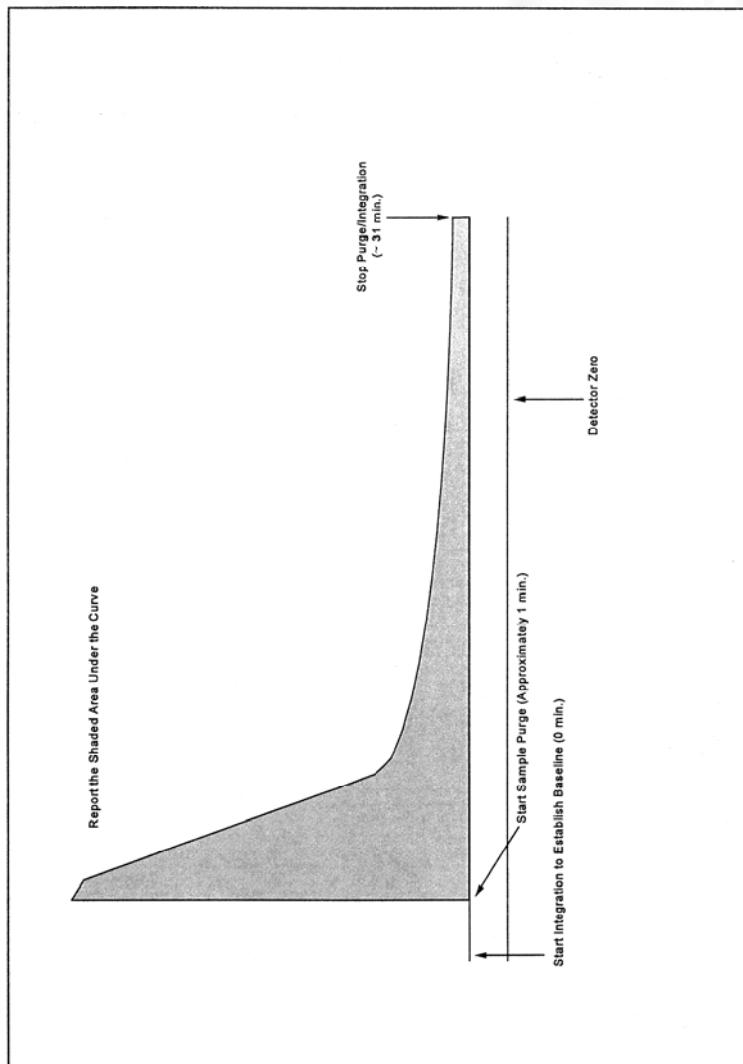


Figure 25D-6. Example Integration of Either Detector.

METHOD 25E—DETERMINATION OF VAPOR PHASE ORGANIC CONCENTRATION IN WASTE SAMPLES

NOTE: Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required.

This method is not inclusive with respect to specifications (e.g., reagents and standards) and calibration procedures. Some material is incorporated by reference from other methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 106, part 61, Appendix B, and Method 18, part 60, Appendix A.

Environmental Protection Agency

Pt. 60, App. A-7, Meth. 25E

1.0 Scope and Application

1.1 Applicability. This method is applicable for determining the vapor pressure of waste cited by an applicable regulation.

1.2 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 The analyst shall select the operating parameters best suited to the requirements for a particular analysis. The analyst shall produce confirming data through an adequate supplemental analytical technique and have the data available for review by the Administrator.

5.0 Safety [Reserved]

6.0 Equipment and Supplies

6.1 Sampling. The following equipment is required:

6.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Numbers 0105-0129 (glass vials), B001-0728 (gray butyl rubber septum, plug style), 0105-0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.1.2 Vial Sealer. Perkin-Elmer Number 105-0106, or equivalent.

6.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

6.1.4 The following equipment is required for sampling.

6.1.4.1 Tap.

6.1.4.2 Tubing. Teflon, 0.25-in. ID.

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

6.1.4.3 Cooling Coil. Stainless steel (304), 0.25 in.-ID, equipped with a thermocouple at the coil outlet.

6.2 Analysis. The following equipment is required.

6.2.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS-6, HS-100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

6.2.2 FID. An FID meeting the following specifications is required.

6.2.2.1 Linearity. A linear response (± 5 percent) over the operating range as demonstrated by the procedures established in section 10.2.

6.2.2.2 Range. A full scale range of 1 to 10,000 parts per million (ppm) propane (C_3H_8). Signal attenuators shall be available to

produce a minimum signal response of 10 percent of full scale.

6.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

6.2.4 Temperature Sensor. Capable of reading temperatures in the range of 30 to 60 °C (86 to 140 °F) with an accuracy of ± 0.1 °C (± 0.2 °F).

7.0 Reagents and Standards

7.1 Analysis. The following items are required for analysis.

7.1.1 Hydrogen (H_2). Zero grade hydrogen, as required by the FID.

7.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon (C) and less than 1 ppm carbon dioxide.

7.1.3 Combustion Gas. Zero grade air or oxygen as required by the FID.

7.2 Calibration and Linearity Check.

7.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall: (a) Certify the gas composition to be accurate to ± 3 percent or better (see section 7.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane 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 the calibration gas in the cylinder by (a) directly analyzing the 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.

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 in accordance with the procedure described in section 7.1 of Method 106 of Part 61, Appendix B, or by (b) calibrating it against 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.

8.0 Sampling Collection, Preservation, Storage, and Transport

8.1 Install a sampling tap to obtain a sample at a point which is most representative of the unexposed waste (where the waste has had minimum opportunity to volatilize to

Pt. 60, App. A-7, Meth. 25E**40 CFR Ch. I (7-1-17 Edition)**

the atmosphere). Assemble the sampling apparatus as shown in Figure 25E-1.

8.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

8.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10 °C

(<50 °F). Fill the sample container halfway (± 5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.

8.4 Alternative sampling techniques may be used upon the approval of the Administrator.

9.0 Quality Control**9.1 Miscellaneous Quality Control Measures.**

Section	Quality control measure	Effect
10.2, 10.3	FID calibration and response check	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Use the procedures in sections 10.2 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.

10.2 Calibration and Linearity. Use the procedures in section 10 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (± 5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three concentrations of calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

10.2.1 Use the procedures in section 11.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in sections 12.3 and 12.2 to test the calibration and the linearity.

10.3 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare 2 calibration standards at the nominal cutoff concentration using the procedures in section 10.2. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E-2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b can be used. Otherwise, use the

procedures in section 10.2 to recalibrate the FID.

11.0 Analytical Procedures

11.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.

11.2 Check the calibration of the FID daily using the procedures in section 10.3.

11.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

11.4 Use the procedures in sections 12.4 and 12.5 to calculate the vapor phase organic vapor pressure in the samples.

11.5 Monitor the output of the detector to make certain that the results are being properly recorded.

12.0 Data Analysis and Calculations**12.1 Nomenclature.**

A = Measurement of the area under the response curve, counts.

b = y-intercept of the linear regression line.

C_s = Measured vapor phase organic concentration of sample, ppm as propane.

C_m = Average measured vapor phase organic concentration of standard, ppm as propane.

C_c = Measured vapor phase organic concentration of standard, ppm as propane.

C_s = Calculated standard concentration, ppm as propane.

k = Slope of the linear regression line.

P_{atm} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).

P* = Organic vapor pressure in the sample, kPa (psi).

PD = Percent difference between the average measured vapor phase organic concentration (C_m) and the calculated standard concentration (C_s).

RSD = Relative standard deviation.

B = 1.333×10^{-7} kPa/[mm Hg(ppm)], (4.91 × 10⁻⁷ psi/[in. Hg(ppm)])

Environmental Protection Agency**Pt. 60, App. A-7, Meth. 25E**

12.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.

$$C_m = kA + b \quad \text{Eq. 25E-1}$$

12.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate PD between C_{ma} and C_s .

The instrument linearity is acceptable if the PD is within five for each standard.

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \quad \text{Eq. 25E-2}$$

12.3. Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \quad \text{Eq. 25E-3}$$

The calibration is acceptable if the RSD is within five for each standard concentration.

12.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.

$$C_a = kA + b \quad \text{Eq. 25E-4}$$

12.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.

$$P^* = \beta P_{bar} C_a \quad \text{Eq. 25E-5}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Salo, Albert E., Samuel Witz, and Robert D. MacPhee. "Determination of Solvent

Vapor Concentrations by Total Combustion Analysis: a Comparison of Infared with Flame Ionization Detectors. Paper No. 75-33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, Massachusetts.

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, Colorado. June 9-13, 1974.) p. 25.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

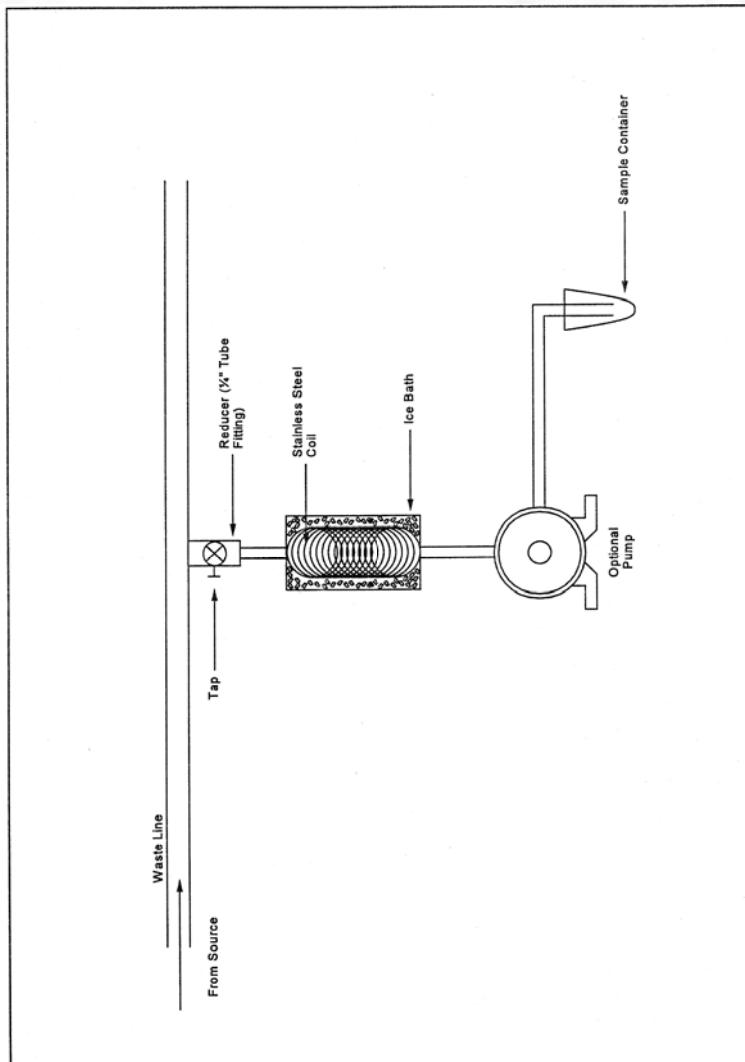


Figure 25E-1. Schematic of Sampling Apparatus

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A-7 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at www.fdsys.gov.

APPENDIX A-8 TO PART 60—TEST
METHODS 26 THROUGH 30B

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

Method 26A—Determination of hydrogen halide and halogen emissions from stationary sources—isokinetic method