

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.

### 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 ( $\pm 5$  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  $\pm 0.1$  °C ( $\pm 0.2$  °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  $\pm 3$  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  $\pm 5$  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  $\pm 5$  percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standards sold.

### 8.0 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

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<sub>s</sub>. 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<sub>a</sub>=Measured vapor phase organic concentration of sample, ppm as propane.

C<sub>ma</sub>=Average measured vapor phase organic concentration of standard, ppm as propane.

C<sub>m</sub>=Measured vapor phase organic concentration of standard, ppm as propane.

C<sub>s</sub>=Calculated standard concentration, ppm as propane.

k=Slope of the linear regression line.

P<sub>bar</sub>=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<sub>m</sub>) and the calculated standard concentration (C<sub>s</sub>).

RSD=Relative standard deviation.

β =1.333 × 10<sup>-7</sup> kPa/[(mm Hg)(ppm)], (4.91 × 10<sup>-7</sup> psi/[(in. Hg)(ppm)])

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## 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.

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

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 Infrared 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

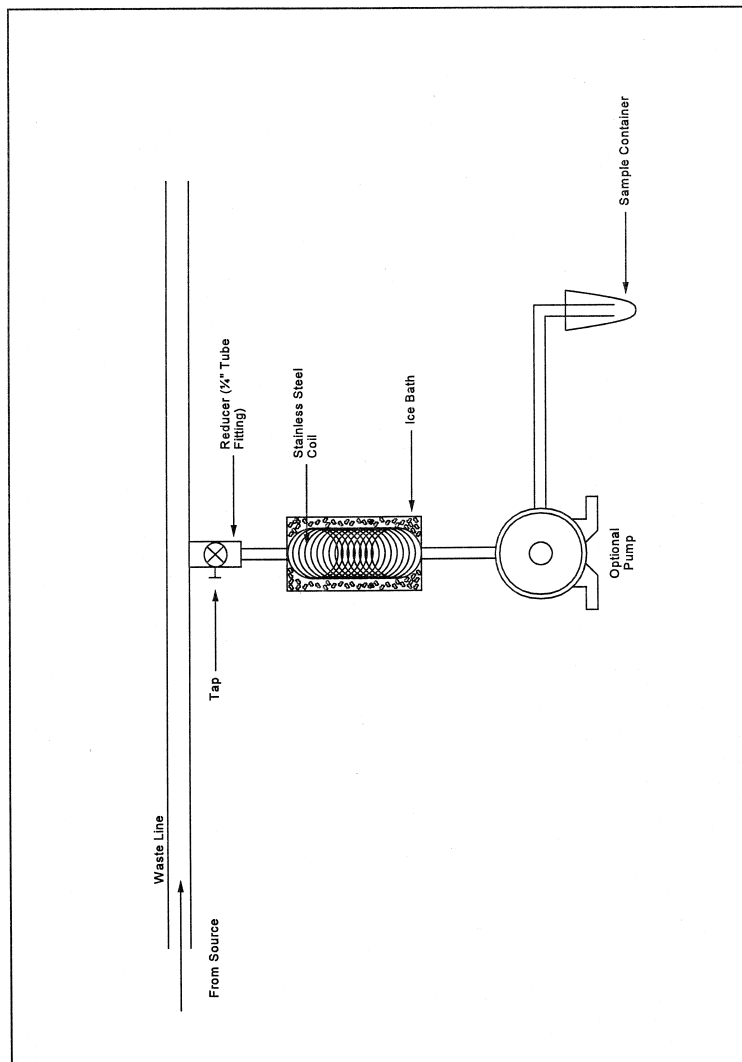


Figure 25E-1. Schematic of Sampling Apparatus

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting part 60, appendix A see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

APPENDIX A-8 TO PART 60—TEST  
METHODS 26 THROUGH 29

Method 26—Determination of Hydrogen Chloride Emissions From Stationary Sources

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