
EMISSION MEASUREMENT TECHNICAL INFORMATION CENTER
CONDITIONAL TEST METHOD

**Determination of Halogenated Organics
from Stationary Sources**

1. INTRODUCTION

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

2. APPLICABILITY AND PRINCIPLE

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

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

3. RANGE AND SENSITIVITY

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

4. INTERFERENCES

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

spectroscopy. This confirming data must be available for review by the Administrator.

5. APPARATUS

5.1 Sampling (see Figure 1). The sampling train consist of the following components:

5.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing (as stack temperature permits), each equipped with a glass wool plug to remove particulate matter. (**Note:** Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency)

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

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

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

5.1.5 Bag Containers. Rigid leak-proof containers for sample bags, with covering to protect contents from sunlight.

5.1.6 Needle Valve. To adjust sample flow rate.

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

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

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

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

5.2 Sample Recovery. Teflon tubing, 6.4-mm outside diameter, to connect bag to gas chromatograph sample loop is required for

~~sample recovery. Use a new unused piece for each series of bag samples that constitutes an emission test and discard upon conclusion of analysis of those bags.~~

5.3 Analysis. The following equipment is needed:

EMTIC CTM-011

EMTIC CONDITIONAL TEST METHOD

Page 3

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

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

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

5.3.4 Gas Regulators. For required gas cylinders.

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

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

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

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

5.3.9 Planimeter. Optional, in place of disc or electronic integrator (Section 5.3.8), to measure chromatograph peak areas.

~~5.4 Calibration. Section 5.4.2 through 5.4.6 are for the optional procedure in Section 8.1.~~

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

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

EMTIC CTM-011

EMTIC CONDITIONAL TEST METHOD

Page 4

5.4.3 Syringes. One 25- μ l and one 50- μ l, gas tight, individually calibrated to dispense liquid halogenated organic solvent.

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

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

6. REAGENTS

It is necessary that all reagents be of chromatographic grade.

6.1 Analysis. The following are needed for analysis:

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

6.1.2 Hydrogen Gas. Zero grade.

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

6.2 Calibration. Use one of the following options: either Sections 6.2.1 and 6.2.2 or Section 6.2.3.

6.2.1 Halogenated Organic Compound, 99 Mol Percent Pure. Certified by the manufacturer to contain a minimum of 99 Mol percent of the particular halogenated organic compound; for use in the preparation of standard gas mixtures as described in Section 8.1

~~6.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 8.1.~~

6.2.3 Cylinder Standards (3). Gas mixture standards (200, 100, and 50 ppm of the halogenated organic compound of interest, in nitrogen). The tester may use these cylinder standards to directly prepare a chromatograph calibration curve as described in Section 8.2.2, if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ± 3 percent or better (See Section 6.2.3.1). (b) the manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value. (c) The manufacturer affixes the date of gas cylinder preparation, certified concentration of the halogenated organic compound, and recommended maximum shelf life to the cylinder before shipment from the gas manufacturer to the buyer.

6.2.3.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the halogenated organic compound in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve. It is recommended that the manufacturer maintain (1) a high-concentration calibration standard (between 200 and 400 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low-concentration calibration standard (between 50 and 100 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the three-point calibration.

6.2.3.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 Mol percent of the halogenated organic compounds) in accordance with the procedure described in Section 7.1 or by (b) having it analyzed by the National Institute of Standards and Technology, if such analysis is available. The agreement between the initially determined concentration value and 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.

~~6.2.4 Audit Cylinder Standards (2). Gas mixture standards with concentrations known only to the person supervising the analysis samples. The audit cylinder standards shall be identically prepared as those in Section 6.2.3 (the halogenated organic compounds of interest, in nitrogen). The concentrations of the audit cylinders should be : one low-concentration cylinder in the range of 25 to 50 ppm, and one high-concentration cylinder in the range of 200 to 300 ppm. When available, audit cylinders may be obtain by contacting: Source Test Audit Coordinator (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711. The request for the audit cylinders must be made at least 30 days prior to the scheduled compliance sample analysis.~~

7. PROCEDURE

7.1 Sampling.

7.1.1 Assemble the sampling train as shown in Figure 1. Perform a bag leak check according to Section 8.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the centroid of the stack and start the pump with the needle valve adjusted to yield a flow that will more than half fill the bag in the specified sample period. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At the time, direct the gas exiting the rotameter away from sampling personnel.

7.1.2 Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect bag container from sunlight.

7.2 **Sample Storage.** Keep the sample bags out of direct sunlight and protect from heat. Perform the analysis within 1 day of sample collection for methylene chloride, ethylene dichloride, and trichlorotrifluoroethane, and within 2 days for

~~perchloroethylene, trichloroethylene, 1,1,1 trichloroethane, and carbon tetrachloride.~~

7.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 0- to 100-ml/min rotameter with flow control valve followed by a charcoal tube and a 0 - 1-in. H₂O pressure gauge. The tester may maintain the sample flow either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

7.4 Analysis. Set the column temperature to 100°C and the detector temperature to 225°C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line

periodically and determine the noise level has stabilized and that base-line drift has ceased. Purge the sample loop for 30 seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carriers gas flow rate, chart speed, and the attenuator setting. Record the barometric pressure. From the chart, note the peak having the retention time corresponding to the halogenated organic compound, as determined in Section 8.2.1. Measure the halogenated organic compound peak area, A_m , by use of a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the peak do not vary more than 5 percent. Use the average value for these two total areas to compute the bag concentration.

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

~~8. PREPARATION OF STANDARD GAS MIXTURES, CALIBRATION, AND QUALITY ASSURANCE.~~

8.1 Preparation of Standard Gas Mixtures. (Optional procedure - delete if cylinder standards are used.) Assemble the apparatus shown in Figure 23-2. Check that all fittings are tight. Evacuate a 50-liter Tedlar or aluminized Mylar Bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. Refer to Table 1. While the bag is filling, use the 50- μ l syringe to inject through the septum on top of the impinger, the quantity required to yield a concentration of 200 ppm. In a like manner, use the 25- μ l syringe to prepare bags having approximately 100- and 50-ppm concentrations. To calculate the specific concentrations, refer to Section 9.1 (Tedlar bag gas mixture standards or methylene chloride, ethylene dichloride, and trichlorotrifluoroethane may be used for 1 day, trichloroethylene and 1,1,1-trichloroethane for 2 days, and perchloroethylene and carbon tetrachloride for 10 days from the date of preparation. (Caution: If the new gas mixture standard is a lower concentration than the previous gas mixture standard, contamination may be a problem when a bag is reused.)

8.2 Calibration.

8.2.1 Determination of Halogenated Organic Compound Retention Time. (This section can be performed simultaneously with Section 8.2.2.) Establish chromatograph conditions identical with those in Section 7.4 above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed, and the attenuator setting. Record peaks and detector responses that occur in the absence of the halogenated organic. Maintain conditions (with the equipment plumbing arranged identically to Section 7.3), flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the halogenated organic compound calibration mixtures, and activate the sample valve. Record the injection time. Select the peak that corresponds to the halogenated organic compound. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the halogenated organic compound peak

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

8.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 6.2.3 or 8.1) using conditions identical with those listed in Sections 7.3 and 7.4. Flush the sampling loop for 30 second at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c , the concentration of halogenated organic injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c , the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two values versus C_c . When the other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points derived by the least squares method. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

8.3 Quality Assurance.

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

8.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks by connecting a water manometer and pressurizing the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 min. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: An alternative leak check method is to pressurize the bag to 5 to 10 cm H_2O 2 to 4 in. H_2O) and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

9. CALCULATIONS

~~9.1 Optional Procedures Standards Concentrations.~~ Calculate each halogenated organic standard concentration (C_c in ppm) prepared in accordance with Section 8.1 as follows:

$$C_c = \frac{24.055 \times 10^3 \frac{B D}{M}}{V_m Y \frac{293}{T_m} \frac{P_m}{760}} \quad \text{Eq. 1}$$

where:

B = Volume of halogenated organic injected, μl .

D = Density of compound at 293°K, g/ml.

M = Molecular weight of compound, g/g-mole.

V_m = Gas volume measured by dry gas matter, liters.

Y = Dry gas meter calibration factor, dimensionless

P_m = Absolute pressure of dry gas meter, mm Hg.

T_m = Absolute temperature of dry gas meter, °K.

24.055 = Ideal molal volume at 293°K and 760 mm Hg, liter/g-mole.

10^3 = Conversion factor, (ppm)(ml)/ μl .

9.2 Sample Concentrations. From the calibration curve described in Section 8.2.2 above, select the value of C_c that corresponds to A_c . Calculate C_s , the concentration of halogenated organic in the sample (in ppm), as follows:

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

where:

C_c = Concentration of the halogenated organic indicated by the gas chromatograph, ppm.

P_r = Reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_r = Sample loop temperature at the time of analysis, °K.

P_i = Laboratory pressure at time of analysis, mm Hg.

T_r = Reference temperature, the sample loop temperature recorded during calibration, °K.

S_{wb} = Water vapor content of the bag sample, fraction.

10. BIBLIOGRAPHY

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

Table 1. Injection Values for Preparation of Standards
(Optional, See Section 8.1)

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