State of Oregon Department of Environmental Quality

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Division 232 Attachments

APPENDIX A–6 TO PART 60—TEST METHODS 16 THROUGH 18

- Method 16—Semicontinuous determination of sulfur emissions from stationary sources
- Method 16A—Determination of total reduced sulfur emissions from stationary sources (impinger technique)
- Method 16B—Determination of total reduced sulfur emissions from stationary sources
- Method 16C—Determination of Total Reduced Sulfur Emissions From Stationary Sources
- Method 17—Determination of particulate emissions from stationary sources (instack filtration method)
- Method 18—Measurement of gaseous organic compound emissions by gas chromatography

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 16—SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

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 have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	50 ppb.
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	50 ppb.
Hydrogen sulfide [H_2S]	7783–06–4	50 ppb.
Methyl mercaptan [CH_4S]	74–93–1	50 ppb.

1.2 Applicability. This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

NOTE: The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

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 emission source and an aliquot is analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as TRS.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Moisture. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120 °C (248 °F). Moisture is removed in the SO_2 scrubber and heating the sample beyond this point is not necessary when the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 Carbon Monoxide (CO) and Carbon Dioxide (CO_2). CO and CO_2 have a substantial desensitizing effect on the flame photometric detector even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 10.2.

4.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by using the Teflon filter after the probe.

4.4 Sulfur Dioxide (SO_2). Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest. The SO_2 scrubber described in section 6.1.3 will effectively remove SO_2 from the sample.

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.

5.2 Hydrogen Sulfide. A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1. Sample Collection. The following items are needed for sample collection.

6.1.1 Probe. Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It must be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. Figure 16–1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes to reduce clogging of the filter and possible adsorption of sample gas. As an alternative, the probe described in section 6.1.1 of Method 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

6.1.2 Particulate Filter. 50–mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120 °C (248 °F).

6.1.3 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (1⁄8 in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0 °C (32 °F). The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH. Connections between the probe, particulate filter, and SO_2 scrubber must be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO_2 scrubber (or alternative point of moisture removal) must be maintained at a temperature of at least 120 °C (248 °F).

6.1.4 Sample Line. Teflon, no greater than 1.3 cm (1⁄2 in.) ID. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

6.1.5 Sample Pump. The sample pump must be a leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis. The following items are needed for sample analysis:

6.2.1 Dilution System. Needed only for high sample concentrations. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

6.2.2 Gas Chromatograph. The gas chromatograph must have at least the following components:

6.2.2.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C (2 °F).

6.2.2.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1 °C (2 °F).

6.2.2.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

6.2.2.4 Flame Photometric Detector.

6.2.2.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

6.2.2.4.2 Power Supply. Capable of delivering up to 750 volts.

6.2.2.4.3 Recorder. Compatible with the output voltage range of the electrometer.

6.2.2.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes must be chosen to provide the needed analytical range. Teflon tubing and fittings must be used throughout to present an inert surface for sample gas. The gas chromatograph must be calibrated with the sample loop used for sample analysis.

6.2.3 Gas Chromatogram Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences. To demonstrate that adequate resolution has been achieved, submit a chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

6.3 Calibration. A calibration system, containing the following components, is required (see Figure 16–2).

6.3.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

6.3.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Flow over the permeation device may also be determined using a soap bubble flowmeter.

6.3.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within 0.1 °C (0.2 °F).

6.3.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within 1 °C (2 °F).

7.0 Reagents and Standards

7.1 Fuel. Hydrogen (H_2), prepurified grade or better.

7.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

7.3 Carrier Gas. Prepurified grade or better.

7.4 Diluent (if required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases

7.5.1 Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer and Sample Line Loss Gas. Same as Method 15, sections 7.6 and 7.7.

8.0 Sample Collection, Preservation, Storage, and Transport

Same as Method 15, section 8.0, except that the references to the dilution system may not be applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.0	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.0	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Same as Method 15, section 10.0, with the following addition and exceptions:

10.1 Use the four compounds that comprise TRS instead of the three reduced sulfur compounds measured by Method 15.

10.2 Flow Meter. Calibration before each test run is recommended, but not required; calibration following each test series is mandatory. Calibrate each flow meter after each complete test series with a wet-test meter. If the flow measuring device differs from the wet-test meter by 5 percent or more, the completed test runs must be voided. Alternatively, the flow data that yield the lower flow measurement may be used. Flow over the permeation device may also be determined using a soap bubble flowmeter.

11.0 Analytical Procedure

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

12.0 Data Analysis and Calculations

12.1 Concentration of Reduced Sulfur Compounds. Calculate the average concentration of each of the four analytes (*i.e.*, DMDS, DMS, H_2S, and MeSH) over the sample run (specified in section 8.2 of Method 15 as 16 injections).

$$C = \frac{\sum_{i=1}^{N} S_i}{N} \qquad \text{Eq. 16-1}$$

Where:

S_i = Concentration of any reduced sulfur compound from the i^{th} sample injection, ppm.

C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.

N = Number of injections in any run period.

12.2 TRS Concentration. Using Equation 16–2, calculate the TRS concentration for each sample run.

$$C_{TRS} = d\sum\left(C_{H_2S} + C_{MeSH} + C_{DMS} + 2C_{DMDS}\right) \qquad \text{Eq. 16-2}$$

Where:

C_{TRS} = TRS concentration, ppmv.

C_{H2S} = Hydrogen sulfide concentration, ppmv.

C_{MeSH} = Methyl mercaptan concentration, ppmv.

C_{DMS} = Dimethyl sulfide concentration, ppmv.

C_{DMDS} = Dimethyl disulfide concentration, ppmv.

d = Dilution factor, dimensionless.

12.3 Average TRS Concentration. Calculate the average TRS concentration for all sample runs performed.

$$\text{Average TRS} = \frac{\sum_{i=1}^{n} \text{TRS}_i}{N(1 - B_{wo})} \qquad \text{Eq. 16-3}$$

Where:

Average TRS = Average total reduced sulfur in ppm.

TRS_i = Total reduced sulfur in ppm as determined by Equation 16–2.

N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases.

13.0 Method Performance

13.1 Analytical Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppmv using 10- to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases.

13.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. O'Keeffe, A.E., and G.C. Ortman. ''Primary Standards for Trace Gas Analysis.'' Analytical Chemical Journal, 38,76. 1966.

2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. ''Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels.'' Environmental Science and Technology, 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. ''An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities.'' Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA. April 6–8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. ''Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds.'' Pulp and Paper Magazine of Canada, 73,3. March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. ''The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van.'' Presented at the 63rd Annual APCA Meeting, St. Louis, MO. June 14–19, 1970.

6. General Reference. Standard Methods of Chemical Analysis, Volumes III-A and III-B Instrumental Methods. Sixth Edition. Van Nostrand Reinhold Co.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

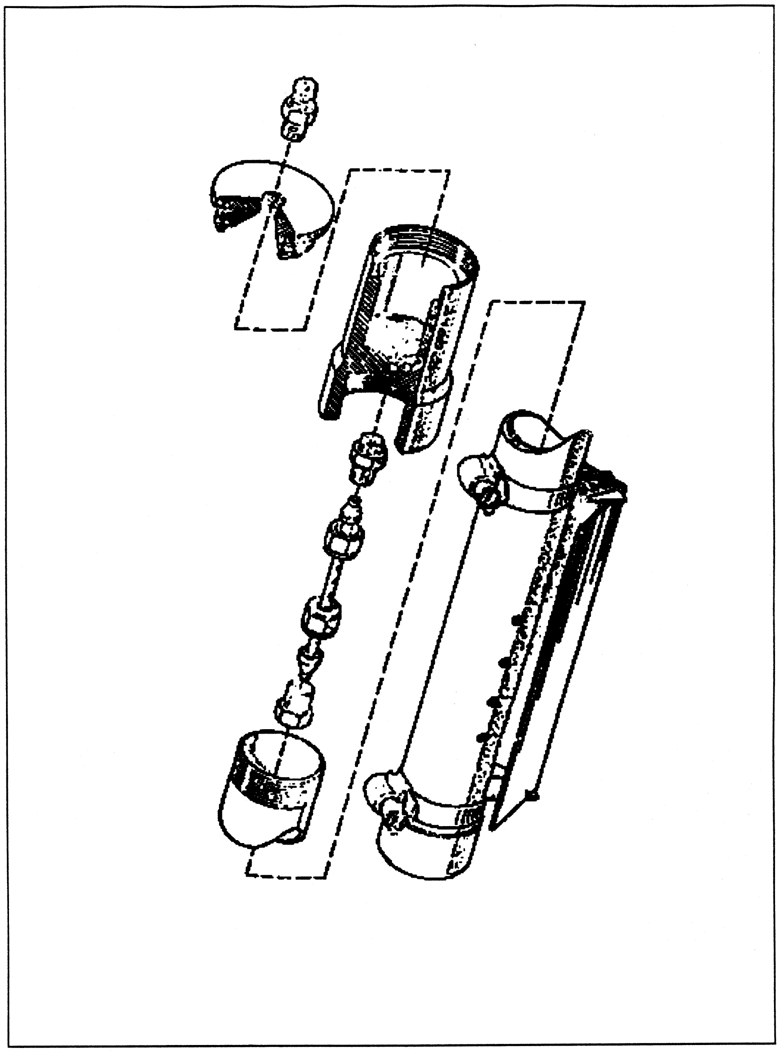

Figure 16-1. Probe used for Sample Gas Containing High Particulate Matter Loading.

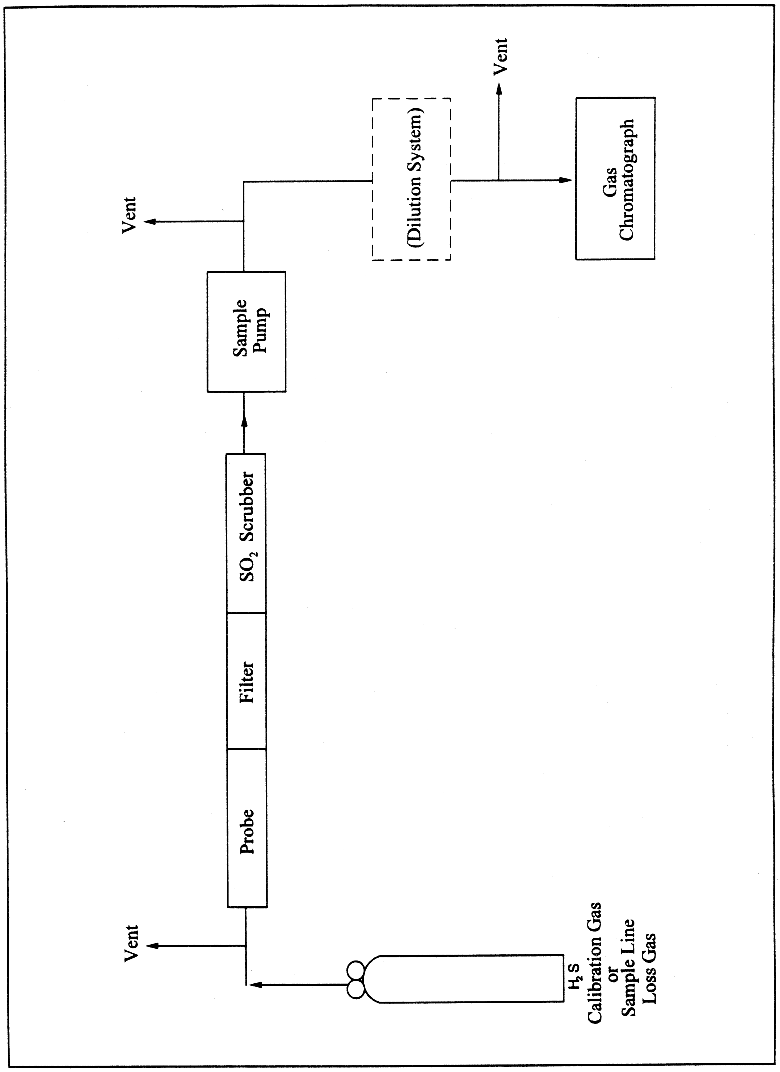

Figure 16-2. Calibration System.

METHOD 16A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES (IMPINGER TECHNIQUE)

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 have a thorough knowledge of at least the following additional test methods: Method 1, Method 6, and Method 16.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total reduced sulfur (TRS) including:	N/A	See section 13.1.
Dimethyl disulfide [$(CH_3)_2S_2$]	62–49–20	
Dimethyl sulfide [$(CH_3)_2S$]	75–18–3	
Hydrogen sulfide [H_2S]	7783–06–4	
Methyl mercaptan [CH_4S]	74–93–1	
Reduced sulfur (RS) including:	N/A	
H_2S	7783–06–4	
Carbonyl sulfide [COS]	463–58–1	
Carbon disulfide [CS_2]	75–15–0	
Reported as: Sulfur dioxide (SO_2)	7449–09–5	

1.2 Applicability. This method is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills, reduced sulfur compounds (H_2S, carbonyl sulfide, and carbon disulfide) from sulfur recovery units at onshore natural gas processing facilities, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2. Note: If sources other than kraft pulp mills experience low oxygen levels in the emissions, the method results may be biased low.

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 An integrated gas sample is extracted from the stack. SO_2 is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO_2, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed prior to oxidation. Furthermore, if the calcium carbonate enters the hydrogen peroxide impingers, the calcium will precipitate sulfate ion. Proper use of the particulate filter described in section 6.1.3 will eliminate this interference.

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.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m^3 will cause lung damage in uninitiated. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.3 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16A–1 and component parts are discussed below. Modifications to this sampling train are acceptable provided the system performance check is met (see section 8.5).

6.1.1 Probe. Teflon tubing, 6.4-mm (¼-in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device should be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼-in.) Teflon elbow (bored out) should be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2.

6.1.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛-in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.1.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.1.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (⅛-in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.1.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90-degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.1.7 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as Method 6, sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midget bubbler of Method 6, section 6.1.1.2 is not required.

6.1.8 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge.

6.1.9 Rate Meter. Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of approximately 2 liters/min (4.2 ft^3/hr).

6.1.10 Volume Meter. Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 liters/min (4.2 ft^3/hr) with an accuracy of 2 percent.

6.2 Sample Recovery. Polyethylene Bottles, 250-ml (one per sample).

6.3 Sample Preparation and Analysis. Same as Method 6, section 6.3, except a 10-ml buret with 0.05-ml graduations is required, and the spectrophotometer is not needed.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Sample Collection. The following reagents are required for sample analysis:

7.1.1 Water. Same as in Method 6, section 7.1.1.

7.1.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.1.3 Hydrogen Peroxide, 3 percent. Same as in Method 6, section 7.1.3 (40 ml is needed per sample).

7.1.4 Recovery Check Gas. Hydrogen sulfide (100 ppmv or less) in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11 or by gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For Method 11, the relative standard deviation should not exceed 5 percent on at least three 20-minute runs.

NOTE: Alternatively, hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (6.4 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

7.1.5 Combustion Gas. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: Diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Flow from a compressed air cylinder is also acceptable.

7.2 Sample Recovery and Analysis. Same as Method 6, sections 7.2.1 and 7.3, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train.

8.1.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor.

8.1.2 For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midget impingers. Leave the third midget impinger empty, and place silica gel in the fourth midget impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Maintain the oxidation furnace at 800 ±100 °C (1472 ±180 °F). Place crushed ice and water around all impingers.

8.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers and bypassing all other sampling train components. A purge rate of 2 liters/min for 10 minutes has been found to be sufficient to obtain equilibrium. After the citrate scrubber has been conditioned, assemble the sampling train, and conduct (optional) a leak-check as described in Method 6, section 8.2.

8.3 Sample Collection. Same as in Method 6, section 8.3, except the sampling rate is 2 liters/min (±10 percent) for 1 or 3 hours. After the sample is collected, remove the probe from the stack, and conduct (mandatory) a post-test leak-check as described in Method 6, section 8.2. The 15-minute purge of the train following collection should not be performed. After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see section 8.5) to determine the reduced sulfur recovery efficiency through the sampling train. After this system performance check and before the next test run, rinse and brush the probe with water, replace the filter, and change the citrate scrubber (optional but recommended).

NOTE: In Method 16, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 16A to be consistent with Method 16, the following may be used to obtain a test run: (1) collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Disconnect the impingers. Quantitatively transfer the contents of the midget impingers of the Method 6 part of the train into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (prior to testing; optional) and (2) to validate a test run (after a run). Perform a check in the field prior to testing consisting of at least two samples (optional), and perform an additional check after each 3 hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of H_2S and comparing the analyzed concentration with the known concentration. Mix the H_2S recovery check gas (Section 7.1.4) and combustion gas in a dilution system such as that shown in Figure 16A–3. Adjust the flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft^3/hr). Use Equation 16A–3 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated.

8.5.3 Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

8.5.4 The recovery check must be performed in the field prior to replacing the SO_2 scrubber and particulate filter and before the probe is cleaned. Use Equation 16A–4 (see section 12.5) to calculate the recovery efficiency. Report the recovery efficiency with the emission data; do not correct the emission data for the recovery efficiency. A sample recovery of 100 ±20 percent must be obtained for the emission data to be valid. However, if the recovery efficiency is not in the 100 ±20 percent range but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensure validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Barium standard solution standardization	Ensure precision of normality determination.
11.1	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Loss Check and Sample Analysis. Same as Method 6, sections 11.1 and 11.2, respectively, with the following exception: for 1-hour sampling, take a 40-ml aliquot, add 160 ml of 100 percent isopropanol and four drops of thorin.

12.0 Data Analysis and Calculations

In the calculations, at least one extra decimal figure should be retained beyond that of the acquired data. Figures should be rounded off after final calculations.

12.1 Nomenclature.

C_{TRS} = Concentration of TRS as SO_2, dry basis corrected to standard conditions, ppmv.
$C_{RG(act)}$ = Actual concentration of recovery check gas (after dilution), ppm.
$C_{RG(m)}$ = Measured concentration of recovery check gas generated, ppm.
C_{H2S} = Verified concentration of H_2S recovery gas.
N = Normality of barium perchlorate titrant, milliequivalents/ml.
P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
Q_{H2S} = Calibrated flow rate of H_2S recovery gas, liters/min.
Q_{CG} = Calibrated flow rate of combustion gas, liters/min.
R = Recovery efficiency for the system performance check, percent.
T_m = Average dry gas meter absolute temperature, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_a = Volume of sample aliquot titrated, ml.
V_m = Dry gas volume as measured by the dry gas meter, liters (dcf).
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, liters (dscf).
V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.
V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).
V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.
Y = Dry gas meter calibration factor.
32.03 = Equivalent weight of sulfur dioxide, mg/meq.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_m Y \frac{T_{std} P_{bar}}{T_m P_{std}} = K_1 Y \frac{V_m P_{bar}}{T_m} \qquad \text{Eq. 16A-1}$$

Where:

K_1 = 0.3855 °K/mm Hg for metric units,
= 17.65 °R/in. Hg for English units.

12.3 Concentration of TRS as ppm SO_2.

$$C_{TRS} = K_2 N \frac{(V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}} \qquad \text{Eq. 16A-2}$$

Where:

$$K_2 = 32.03\frac{\text{mg}}{\text{meq}}\frac{24.05\text{L}}{\text{mole}}\frac{1\,\text{mole}}{64.06\text{g}}\frac{1\text{g}}{10^3\,\text{mg}}\frac{10^3\,\text{mL}}{\text{L}}\frac{10^3\,\mu\text{L}}{\text{lmL}}$$
$$= \frac{12025\,\mu\text{L}}{\text{meq}}$$

12.4 Concentration of Recovery Gas Generated in the System Performance Check.

$$C_{RG} = \frac{Q_{H_2S}\,C_{H_2S}}{Q_{H_2S} + Q_{CG}} \qquad \text{Eq. 16A-3}$$

12.5 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \qquad \text{Eq. 16A-4}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv SO_2 when sampling at 2 liters/min (4.2 ft^3/hr) for 3 hours or 0.3 ppmv when sampling at 2 liters/min (4.2 ft^3/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision. Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

13.3 Bias.

13.3.1 No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16 at a lime kiln indicated that there was no bias in Method 16A. However, instability of the source emissions adversely affected the comparison. The precision of Method 16A at the lime kiln was similar to that obtained at the recovery boiler (Section 13.2.1).

13.3.3 Relative standard deviations of 2.7 and 7.7 percent have been obtained for system performance checks.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

As an alternative to the procedures specified in section 7.1.4, the following procedure may be used to verify the H_2S concentration of the recovery check gas.

16.1 Summary. The H_2S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range. The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences. There are no known interferences to this procedure when used to analyze cylinder gases containing H_2S in nitrogen.

16.4 Precision and Bias. Laboratory tests have shown a relative standard deviation of less than 3 percent. The procedure showed no bias when compared to a gas chromatographic method that used gravimetrically certified permeation tubes for calibration.

16.5 Equipment and Supplies.

16.5.1 Sampling Apparatus. The sampling train is shown in Figure 16A–4. Its component parts are discussed in sections 16.5.1.1 through 16.5.2.

16.5.1.1 Sampling Line. Teflon tubing (¼-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve. Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers. Three impingers of approximately 100-ml capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The impinger bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 6.4-mm (¼-in.) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1.27 cm (½ in.) from the bottom (Southern Scientific, Inc., Micanopy, Florida: Set Number S6962–048). The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer. Same as Method 11, sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator. Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter. Calibrated for 100 and 500 ml, or two separate bubble meters.

16.5.1.7 Critical Orifice. For volume and rate measurements. The critical orifice may be fabricated according to section 16.7.3 and must be calibrated as specified in section 16.12.4.

16.5.1.8 Graduated Cylinder. 50-ml size.

16.5.1.9 Volumetric Flask. 1-liter size.

16.5.1.10 Volumetric Pipette. 15-ml size.

16.5.1.11 Vacuum Gauge. Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch.

16.5.2 Sample Recovery and Analysis.

16.5.2.1 Erlenmeyer Flasks. 125- and 250-ml sizes.

16.5.2.2 Pipettes. 2-, 10-, 20-, and 100-ml volumetric.

16.5.2.3 Burette. 50-ml size.

16.5.2.4 Volumetric Flask. 1-liter size.

16.5.2.5 Graduated Cylinder. 50-ml size.

16.5.2.6 Wash Bottle.

16.5.2.7 Stirring Plate and Bars.

16.6 Reagents and Standards. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

16.6.1 Water. Same as Method 11, section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution. Dissolve 20 g zinc acetate in water, and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [$KH(IO_3)_2$] Solution, Standard 0.100 N. Dissolve 3.249 g anhydrous $KH(IO_3)_2$ in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate ($Na_2S_2O_3$) Solution, Standard 0.1 N. Same as Method 11, section 7.3.2. Standardize according to section 16.12.2.

16.6.5 $Na_2S_2O_3$ Solution, Standard 0.01 N. Pipette 100.0 ml of 0.1 N $Na_2S_2O_3$ solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N. Same as Method 11, section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N. Same as in Method 11, section 7.2.4. Standardize according to section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight. Add 230 ml concentrated HCl (specific gravity 1.19) to 770 ml water.

16.6.9 Starch Indicator Solution. To 5 g starch (potato, arrowroot, or soluble), add a little cold water, and grind in a mortar to a thin paste. Pour into 1 liter of boiling water, stir, and let settle overnight. Use the clear supernatant. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide per liter of starch solution. Some commercial starch substitutes are satisfactory.

16.7 Pre-test Procedures.

16.7.1 Selection of Gas Sample Volumes. This procedure has been validated for estimating the volume of cylinder gas sample needed when the H_2S concentration is in the range of 5 to 1500 ppmv. The sample volume ranges were selected in order to ensure a 35 to 60 percent consumption of the 20 ml of 0.01 N iodine (thus ensuring a 0.01 N $Na_2S_2O_3$ titer of approximately 7 to 12 ml). The sample volumes for various H_2S concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the H_2S concentration stated by the manufacturer. For example, for analyzing a cylinder gas containing approximately 10 ppmv H_2S, the optimum sample volume is 65 liters (650 ppm-liters/10 ppmv). For analyzing a cylinder gas containing approximately 1000 ppmv H_2S, the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppmv).

Approximate cylinder gas H_2S concentration (ppmv)	Approximate ppm-liters desired
5 to <30	650
30 to <500	800
500 to <1500	1000

16.7.2 Critical Orifice Flow Rate Selection. The following table shows the ranges of sample flow rates that are desirable in order to ensure capture of H_2S in the impinger solution. Slight deviations from these ranges will not have an impact on measured concentrations.

Cylinder gas H_2S concentration (ppmv)	Critical orifice flow rate (ml/min)
5 to 50 ppmv	1500 ±500
50 to 250 ppmv	500 ±250
250 to <1000 ppmv	200 ±50
>1000 ppmv	75 ±25

16.7.3 Critical Orifice Fabrication. Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting 1⁄16-in. × 1⁄4-in. (0.16 cm × 0.64 cm) reducing fittings to both ends. The inside diameters and lengths of orifice tubes needed to obtain specific flow rates are shown below.

Tube (in. OD)	Tube (in. ID)	Length (in.)	Flowrate (ml/min)	Altech Catalog No.
1⁄16	0.007	1.2	85	301430
1⁄16	0.01	3.2	215	300530
1⁄16	0.01	1.2	350	300530
1⁄16	0.02	1.2	1400	300230

16.7.4 Determination of Critical Orifice Approximate Flow Rate. Connect the critical orifice to the sampling system as shown in Figure 16A–4 but without the H_2S cylinder. Connect a rotameter in the line to the first impinger. Turn on the pump, and adjust the valve to give a reading of about half atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable flow rate is reached, and record this as the critical vacuum. The measured flow rate indicates the expected critical flow rate of the orifice. If this flow rate is in the range shown in section 16.7.2, proceed with the critical orifice calibration according to section 16.12.4.

16.7.5 Determination of Approximate Sampling Time. Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in section 16.7.1.

$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A–4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A–4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut, to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N $Na_2S_2O_3$ until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

NOTE: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30 to 45 seconds after the titration endpoint is reached. This should not be taken to mean the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N $Na_2S_2O_3$. Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in section 16.12.4. If the Q_{std} obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, sections 10.1.3 and 10.1.4.

16.12.2 $Na_2S_2O_3$ Solution, 0.1 N. Standardize the 0.1 N $Na_2S_2O_3$ solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H_2SO_4, 10.0 ml of 0.100 N $KH(IO_3)_2$

and 1 g potassium iodide. Titrate immediately with 0.1 N $Na_2S_2O_3$ until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of $Na_2S_2O_3$ consumed to calculate the normality to three decimal figures using Equation 16A–5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N $Na_2S_2O_3$ solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat the titration until replicate values agree within 0.05 ml. Take the average volume to calculate the normality to three decimal figures using Equation 16A–6.

16.12.4 Critical Orifice. Calibrate the critical orifice using the sampling train shown in Figure 16A–4 but without the H_2S cylinder and vent rotameter. Connect the soap bubble meter to the Teflon line that is connected to the first impinger. Turn on the pump, and adjust the needle valve until the vacuum is higher than the critical vacuum determined in section 16.7.4. Record the time required for gas flow to equal the soap bubble meter volume (use the 100-ml soap bubble meter for gas flow rates below 100 ml/min, otherwise use the 500-ml soap bubble meter). Make three runs, and record the data listed in Table 16A–1. Use these data to calculate the volumetric flow rate of the orifice.

16.13 Calculations.

16.13.1 Nomenclature.

B_{wa} = Fraction of water vapor in ambient air during orifice calibration.

C_{H_2S} = H_2S concentration in cylinder gas, ppmv.

$$K_2 = 32.03\frac{\text{mg}}{\text{meq}}\frac{24.05\text{L}}{\text{mole}}\frac{1\,\text{mole}}{64.06\text{g}}\frac{1\text{g}}{10^3\text{mg}}\frac{10^3\text{mL}}{\text{L}}\frac{10^3\mu\text{L}}{1\,\text{mL}} = \frac{12025\,\mu\text{L}}{\text{meq}}$$

M_a = Molecular weight of ambient air saturated at impinger temperature, g/g-mole.

M_s = Molecular weight of sample gas (nitrogen) saturated at impinger temperature, g/g-mole.

NOTE: (For tests carried out in a laboratory where the impinger temperature is 25 °C, M_a = 28.5 g/g-mole and M_s = 27.7 g/g-mole.)

N_I = Normality of standard iodine solution (0.01 N), g-eq/liter.

N_T = Normality of standard $Na_2S_2O_3$ solution (0.01 N), g-eq/liter.

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

Q_{std} = Average volumetric flow rate through critical orifice, liters/min.

T_{amb} = Absolute ambient temperature, °K.

T_{std} = Standard absolute temperature, 293 °K.

θ_s = Sampling time, min.

θ_{sb} = Time for soap bubble meter flow rate measurement, min.

$V_{m(std)}$ = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

V_{sb} = Volume of gas as measured by the soap bubble meter, ml.

$V_{sb(std)}$ = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, liters.

V_I = Volume of standard iodine solution (0.01 N) used, ml.

V_T = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used, ml.

V_{TB} = Volume of standard $Na_2S_2O_3$ solution (0.01 N) used for the blank, ml.

16.13.2 Normality of Standard $Na_2S_2O_3$ Solution (0.1 N).

$$N_T = \frac{1}{\text{mL}\,Na_2S_2O_3\,\text{consumed}} \qquad \text{Eq. 16A-5}$$

16.13.3 Normality of Standard Iodine Solution (0.01 N).

$$N_I = \frac{N_T V_T}{V_I} \qquad \text{Eq. 16A-6}$$

16.13.4 Sample Gas Volume.

$$V_{m(std)} = \overline{Q}_{std} \Theta_s \left(1 - B_{wa}\right) \frac{M_a}{M_b} \qquad \text{Eq. 16A-7}$$

16.13.5 Concentration of H_2S in the Gas Cylinder.

17.0 References

$$C_{H_2S} = \frac{K N_T \left(V_{TB} - V_T\right)}{V_{m(std)}} \qquad \text{Eq. 16A-8}$$

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9. National Council of the Paper Industry for Air and Stream Improvement. Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Technical Bulletin Number 450. New York, NY. January 1985. 23 pp.

10. National Council of the Paper Industry for Air and Stream Improvement. Modified Wet Chemical Method for Determining the H_2S Concentration of Calibration Cylinder Gases. Draft Report. New York, NY. March 1987. 29 pp.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

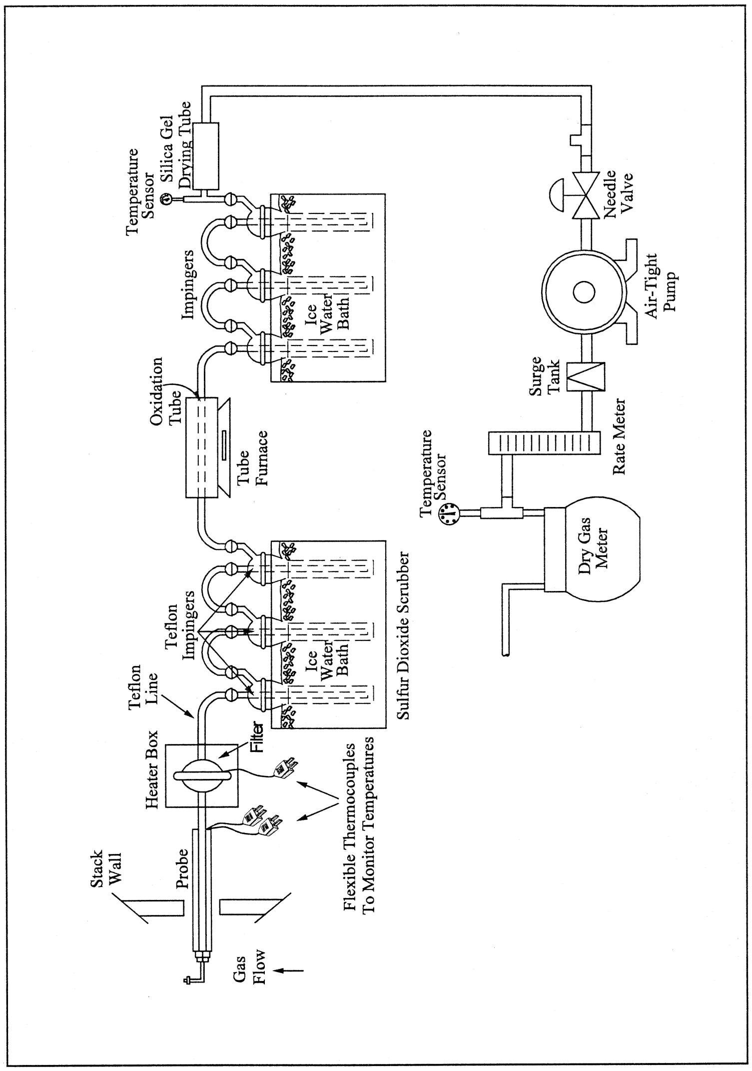

Figure 16A-1. Sampling Train.

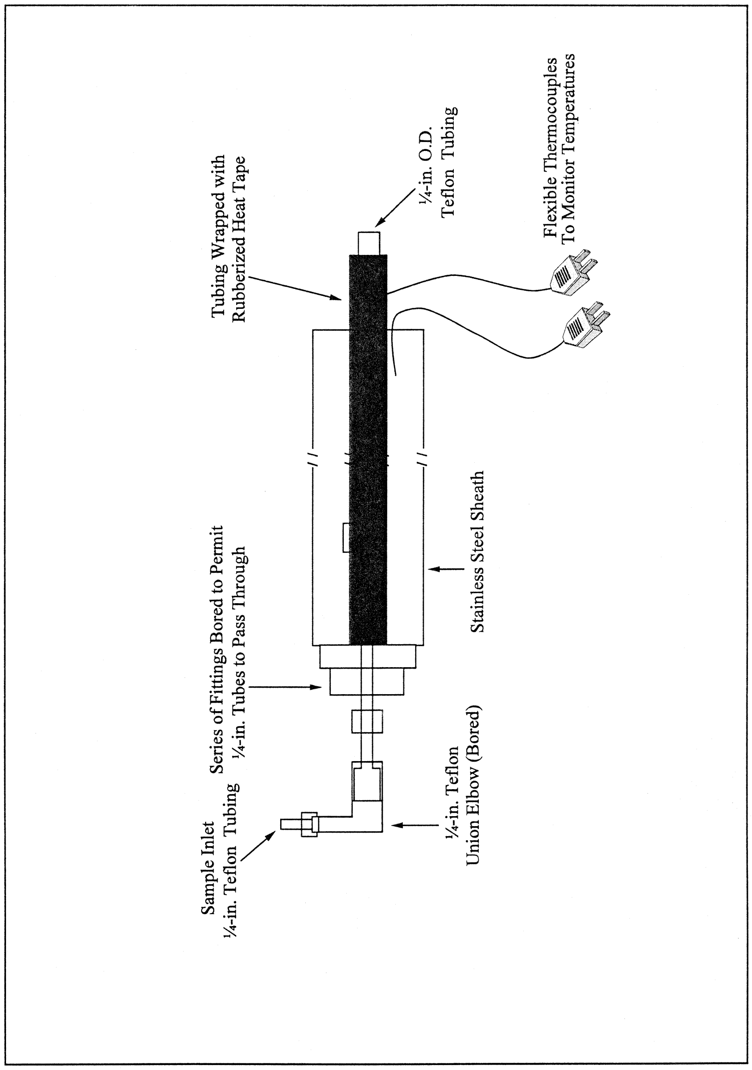

Figure 16A-2. Angled Sampling Probe.

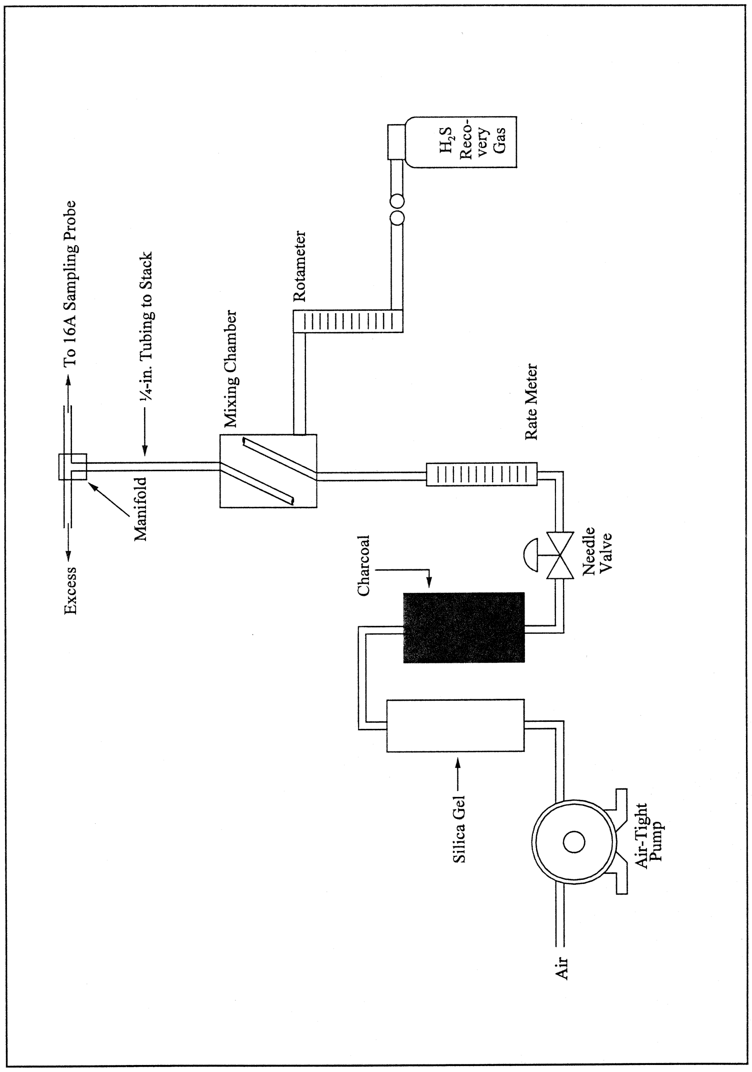

Figure 16A-3. Recovery Gas Dilution System.

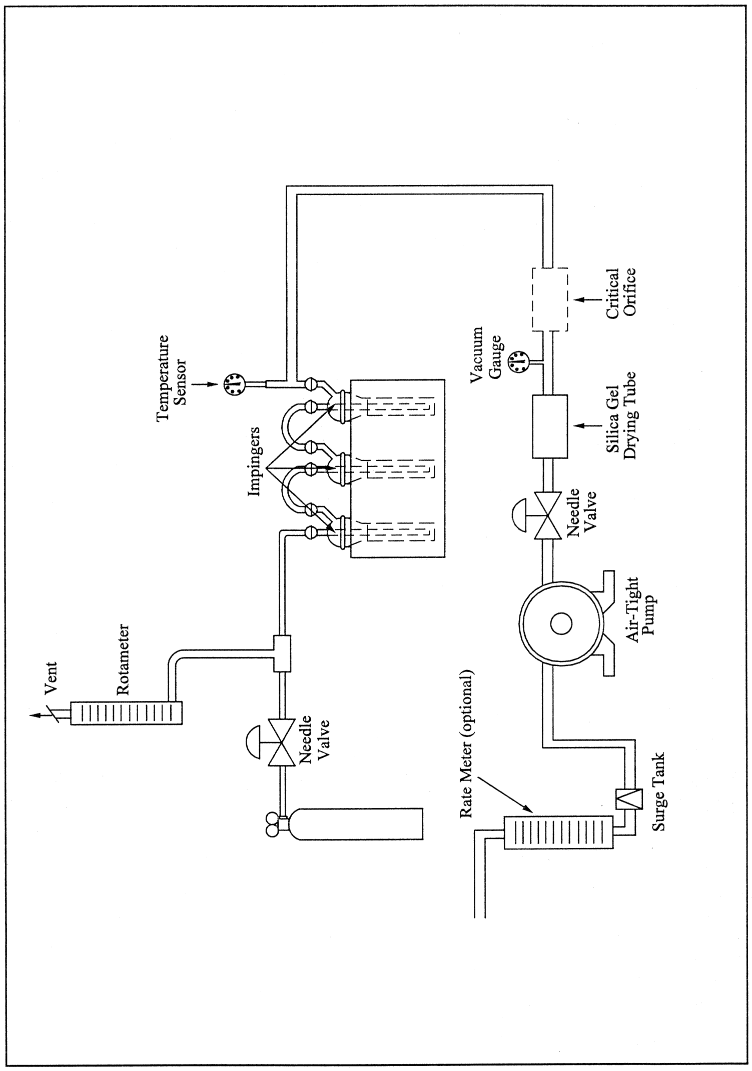

Figure 16A-4. Recovery Check Gas Sampling Train.

Date ____________________
Critical orifice ID ____________________
Soap bubble meter volume, Vsb____ liters
Time, θsb
Run no. 1 ____ min ____ sec
Run no. 2 ____ min ____ sec
Run no. 3 ____ min ____ sec
Average ____ min ____ sec
Covert the seconds to fraction of minute:
Time=____ min + ____ Sec/60=____ min

Barometric pressure, P_{bar}=____ mm Hg
Ambient temperature, t_{amb} = 273 + ____ °C=____ °K=____ mm Hg. (This should be approximately 0.4 times barometric pressure.)
Pump vacuum,

$$V_{sb(std)} = \frac{V_{sb}\,T_{std}\,P_{bar}\left(10^{-3}\right)}{T_{amb}\,P_{std}}$$

$$= \text{----------}\ \text{liters}$$

$$Q_{std} = \frac{V_{sb(std)}}{\Theta_{sb}}$$

$$= \text{----------}\ \text{liters/min}$$

Table 16A–1. Critical Orifice Calibration Data

METHOD 16B—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

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 have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Total reduced sulfur (TRS) including:	N/A
Dimethyl disulfide (DMDS), [$(CH_3)_2S_2$]	62–49–20
Dimethyl sulfide (DMS), [$(CH_3)_2S$]	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), [CH_4S]	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO_2.

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 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and analyzed as SO_2 by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

4.3 Carbon monoxide (CO) and carbon dioxide (CO_2) have substantial desensitizing effects on the FPD even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before the SO_2. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms should show agreement within the precision limits of section 13.0.

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.

5.2 Hydrogen Sulfide (H_2S). A flammable, poisonous gas with the odor of rotten eggs. H_2S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16B–1. Modifications to the apparatus are accepted provided the system performance check in section 8.4.1 is met.

6.1.1 Probe, Probe Brush, Particulate Filter, SO_2 Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump. Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis.

6.2.1 Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatograph Columns. Same as in Method 16, section 6.2.3. Other columns with demonstrated ability to resolve SO_2 and be free from known interferences are acceptable alternatives. Single column systems such as a 7-ft Carbsorb B HT 100 column have been found satisfactory in resolving SO_2 from CO_2.

7.0 Reagents and Standards

Same as in Method 16, section 7.0, except for the following:

7.1 Calibration Gas. SO_2 permeation tube gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. In place of SO_2 permeation tubes, cylinder gases containing SO_2 in nitrogen may be used for calibration. The cylinder gas concentration must be verified according to section 8.2.1 of Method 6C. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

7.2 Recovery Check Gas.

7.2.1 Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in section 16.0 of Method 16A, or gas chromatography where the instrument is calibrated with an H_2S permeation tube as described below. For the wet-chemical methods, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

7.2.2 Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (64 ft^3/hr), an H_2S concentration in the range of the stack gas or within 20 percent of the emission standard can be generated.

7.3 Combustion Gas. Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Gas from a compressed air cylinder is also acceptable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures. Same as in Method 15, section 8.1.

8.2 Sample Collection. Before any source sampling is performed, conduct a system performance check as detailed in section 8.4.1 to validate the sampling train components and procedures. Although this test is optional, it would significantly reduce the possibility of rejecting tests as a result of failing the post-test performance check. At the completion of the pretest system performance check, insert the sampling probe into the test port making certain that no dilution air enters the stack though the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the dilution factor as in section 10.4 of Method 15.

8.3 Analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of SO_2 directly from the calibration curves or from the equation for the least-squares line.

8.4. Post-Test Procedures

8.4.1 System Performance Check. Same as in Method 16A, section 8.5. A sufficient number of sample injections should be made so that the precision requirements of section 13.2 are satisfied.

8.4.2 Determination of Calibration Drift. Same as in Method 15, section 8.3.2.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 8.3	System performance check	Ensure validity of sampling train components and analytical procedure.
8.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Analytical calibration	Ensure precision of analytical results within 5 percent.

10.0 Calibration

Same as in Method 16, section 10, except SO_2 is used instead of H_2S.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{SO2} = Sulfur dioxide concentration, ppmv.
C_{TRS} = Total reduced sulfur concentration as determined by Equation 16B–1, ppmv.
d = Dilution factor, dimensionless.
N = Number of samples.

12.2 SO_2 Concentration. Determine the concentration of SO_2, C_{SO2}, directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

12.3 TRS Concentration.

$$C_{TRS} = C_{SO_2} d \qquad \text{Eq. 16B-1}$$

12.4 Average TRS Concentration

$$\text{Avg.}C_{TRS} = \frac{\sum_{i=1}^{n} C_{TRS}}{N} \qquad \text{Eq. 16B-2}$$

13.0 Method Performance.

13.1 Range and Sensitivity. Coupled with a GC using a 1-ml sample size, the maximum limit of the FPD for SO_2 is approximately 10 ppmv. This limit is extended by diluting the sample gas before analysis or by reducing the sample aliquot size. For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size.

13.2 GC/FPD Calibration and Precision. A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

13.3 Calibration Drift. The calibration drift determined from the mean of the three injections made at the beginning and end of any run or series of runs within a 24-hour period must not exceed 5 percent.

13.4 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

13.5 Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Same as in Method 16, section 16.0.

2. National Council of the Paper Industry for Air and Stream Improvement, Inc, A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.

3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

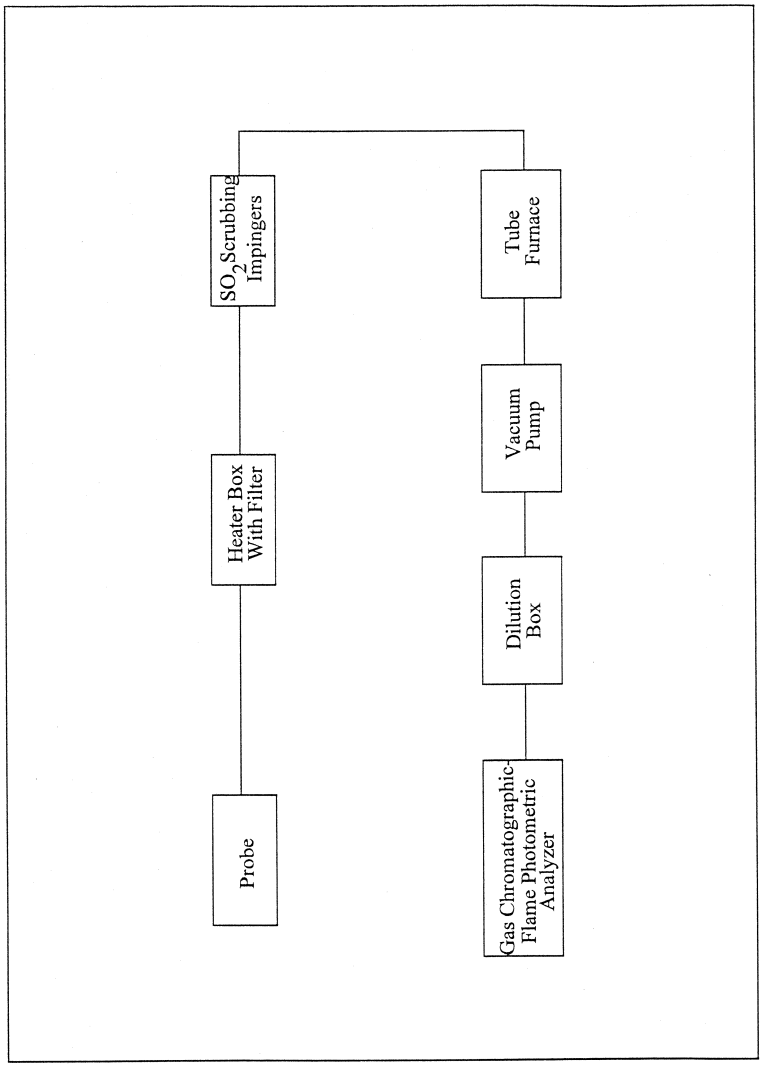

Figure 16B-1. Method 16B Sampling Train.

Method 16C—Determination of Total Reduced Sulfur Emissions From Stationary Sources

1.0 Scope and Application

What is Method 16C?

Method 16C is a procedure for measuring total reduced sulfur (TRS) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

(a) Method 6C—Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(b) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

(c) Method 16A—Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)

1.1 Analytes. What does Method 16C determine?

Analyte	CAS No.
Total reduced sulfur including:	N/A
Dimethyl disulfide (DMDS), $[(CH_3)_2S_2]$	62–49–20
Dimethyl sulfide (DMS), $[(CH_3)_2S]$	75–18–3
Hydrogen sulfide (H_2S)	7783–06–4
Methyl mercaptan (MeSH), (CH_4S)	74–93–1
Reported as: Sulfur dioxide (SO_2)	7449–09–5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations.

1.3 Data Quality Objectives. Adherence to the requirements described in Method 16C will enhance the quality of the data obtained.

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack. The SO_2 is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO_2 and determined as SO_2 by an instrumental analyzer. This method is a combination of the sampling procedures of Method 16A and the analytical procedures of Method 6C (referenced in Method 7E), with minor modifications to facilitate their use together.

3.0 Definitions

Analyzer calibration error, Calibration curve, Calibration gas, Low-level gas, Mid-level gas, High-level gas, Calibration drift, Calibration span, Data recorder, Direct calibration mode, Gas analyzer, Interference check, Measurement system, Response time, Run, System calibration mode, System performance check, and *Test* are the same as used in Methods 16A and 6C.

4.0 Interferences

4.1 Reduced sulfur compounds other than those defined as TRS, if present, may be measured by this method. Compounds like carbonyl sulfide, which is partially oxidized to SO_2 and may be present in a lime kiln exit stack, would be a positive interferent. Interferences may vary among instruments, and instrument-specific interferences must be evaluated through the interference check.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H_2S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

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 to establish appropriate safety and health practices before performing this test method.

5.2 Hydrogen Sulfide. Hydrogen sulfide is a flammable, poisonous gas with the odor of rotten eggs. Hydrogen sulfide is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure. It is the responsibility of the user of this test method to establish appropriate safety and health practices.

6.0 Equipment and Supplies

What do I need for the measurement system?

The measurement system is similar to those applicable components in Methods 16A and 6C. Modifications to the apparatus are accepted provided the performance criteria in section 13.0 are met.

6.1 Probe. Teflon tubing, 6.4-mm (¼ in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device must be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe must be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent moisture and particulate from entering between the probe and sheath. A 6.4-mm (¼ in.) Teflon elbow (bored out) must be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing must be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A–2 of Method 16A.

6.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (⅛ in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-μm porosity, Teflon filter (may be available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343, or other suppliers of filters). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.4 SO_2 Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing may be available through Savillex or other suppliers.) The first two impingers contain 100 ml of citrate buffer, and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3 mm (1/8 in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.5 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (1/4 in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternative combustion tubes are acceptable provided they are shown to combust TRS at concentrations encountered during tests.

6.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 ±100 °C (1472 ±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.7 Sampling Pump. A leak-free pump is required to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system and must be constructed of material that is non-reactive to the gas it contacts. For dilution-type measurement systems, an eductor pump may be used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.8 Calibration Gas Manifold. The calibration gas manifold must allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system must be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe, and a probe controller is needed to maintain the proper dilution ratio.

6.9 Sample Gas Manifold. The sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer. The manifold must be made of material that is non-reactive to SO_2 and be configured to safely discharge the bypass gas.

6.10 SO_2 Analyzer. You must use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO_2 in the gas stream provided it meets the performance specifications in section 13.0.

6.11 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data must be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. When such specifications are not available, the best available grade must be used.

7.1 Water. Deionized distilled water must conform to ASTM Specification D 1193–77 or 91 Type 3 (incorporated by reference—see §60.17). The $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.3 Calibration Gas. Refer to section 7.1 of Method 7E (as applicable) for the calibration gas requirements. Example calibration gas mixtures are listed below.

(a) SO_2 in nitrogen (N_2).
(b) SO_2 in air.
(c) SO_2 and carbon dioxide (CO_2) in N_2.
(d) SO_2 and oxygen (O_2) in N_2.
(e) $SO_2/CO_2/O_2$ gas mixture in N_2.
(f) CO_2/NO_X gas mixture in N_2.
(g) $CO_2/SO_2/NO_X$ gas mixture in N_2.

For fluorescence-based analyzers, the O_2 and CO_2 concentrations of the calibration gases as introduced to the analyzer must be within 1.0 percent (absolute) O_2 and 1.0 percent (absolute) CO_2 of the O_2 and CO_2 concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO_2 in air and the nomographs provided by the vendor to determine the quenching correction factor (the effluent O_2 and CO_2 concentrations must be known). This requirement does not apply to ambient-level fluorescence analyzers that are used in conjunction with sample dilution systems. Alternatively, H_2S in O_2 or air may be used to calibrate the analyzer through the tube furnace.

7.4 System Performance Check Gas. You must use H_2S (100 ppmv or less) stored in aluminum cylinders with the concentration certified by the manufacturer. Hydrogen sulfide in nitrogen is more stable than H_2S in air, but air may be used as the balance gas.

NOTE: Alternatively, H_2S recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at the appropriate dilution gas flow rate, an H_2S concentration can be generated in the range of the stack gas or within 20 percent of the emission standard.

7.5 Interference Check. Examples of test gases for the interference check are listed in Table 7E–3 of Method 7E.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pre-sampling Tests. Before measuring emissions, perform the following procedures:

(a) Calibration gas verification,

(b) Calibration error test,

(c) System performance check,

(d) Verification that the interference check has been satisfied.

8.1.1 Calibration Gas Verification. Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.1.2 Analyzer Calibration Error Test. After you have assembled, prepared, and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test before the first run and again after any failed system performance check or failed drift test to ensure the calibration is acceptable. Introduce the low-, mid-, and high-level calibration gases sequentially to the analyzer in direct calibration mode. For each calibration gas, calculate the analyzer calibration error using Equation 16C–1 in section 12.2. The calibration error for the low-, mid-, and high-level gases must not exceed 5.0 percent or 0.5 ppmv. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.1.3 System Performance Check. A system performance check is done (1) to validate the sampling train components and procedure (prior to testing), and (2) to validate a test run (after a run). You must conduct a performance check in the field prior to testing, and after each 3-hour run or after three 1-hour runs. A performance check consists of sampling and analyzing a known concentration of H_2S (system performance check gas) and comparing the analyzed concentration to the known concentration. To conduct the system performance check, mix the system performance check gas (Section 7.4) and ambient air, that has been conditioned to remove moisture and sulfur-containing gases, in a dilution system such as that shown in Figure 16A–3 of Method 16A. Alternatively, ultra-high purity (UHP) grade air may be used. Adjust the gas flow rates to generate an H_2S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft3/hr). Use Equation 16A–3 from Method 16A to calculate the concentration of system performance check gas generated. Calibrate the flow rate from both gas sources with a soap bubble flow meter so that the diluted concentration of H_2S can be accurately calculated. Alternatively, mass flow controllers with documented calibrations may be used if UHP grade air is being used. Sample duration should be sufficiently long to ensure a stable response from the analyzer. Analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or other suitable device that will ensure extraction of a representative sample. The TRS sample concentration measured between system performance checks is corrected by the average of the pre- and post-system performance checks.

8.1.4 Interference Check. Same as in Method 7E, section 8.2.7.

8.2 Measurement System Preparation.

8.2.1 For the SO_2 scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor. Prepare the oxidation furnace and maintain at 800 ±100 °C (1472 ±180 °F).

8.2.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers as described in section 8.4.1.

8.3 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures must be completed before sampling is initiated.

8.3.1 Leak-Check. Appropriate leak-check procedures must be employed to verify the integrity of all components, sample lines, and connections. For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

8.3.2 Initial System Performance Check. A system performance check using the test gas (Section 7.4) is performed prior to testing to validate the sampling train components and procedure.

8.4 Sample Collection and Analysis.

8.4.1 After performing the required pretest procedures described in section 8.1, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Condition the sampling system and citrate buffer solution for a minimum of 15 minutes before beginning analysis. Begin sampling and analysis. A source test consists of three test runs. A test run shall consist of a single sample collected over a 3-hour period or three separate 1-hour samples collected over a period not to exceed six hours.

8.5 Post-Run Evaluations.

8.5.1 System Performance Check. Perform a post-run system performance check before replacing the citrate buffer solution and particulate filter and before the probe is cleaned. The check results must not exceed the 100 ±20 percent limit set forth in section 13.2. If this limit is exceeded, the intervening run is considered invalid. However, if the recovery efficiency is not in the 100 ±20 percent range, but the results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test.

8.5.2 Calibration Drift. After a run or series of runs, not to exceed a 24-hour period after initial calibration, perform a calibration drift test using a calibration gas (preferably the level that best approximates the sample concentration) in direct calibration mode. This drift must not differ from the initial calibration error percent by more than 3.0 percent or 0.5 ppm. If the drift exceeds this limit, the intervening run or runs are considered valid, but a new analyzer calibration error test must be performed and passed before continuing sampling.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Analyzer calibration error test	Establishes initial calibration accuracy within 5.0%.
8.1.3, 8.5.1	System performance check	Ensures accuracy of sampling/analytical procedure to 100 ±20%.
8.5.2	Calibration drift test	Ensures calibration drift is within 3.0%.
8.1.4	Interference check	Checks for analytical interferences.
8.3	Sampling equipment leak-check	Ensures accurate measurement of sample gas flow rate, sample volume.

10.0 Calibration

10.1 Calibrate the system using the gases described in section 7.3. Perform the initial 3-point calibration error test as described in section 8.1.2 before you start the test. The specification in section 13 must be met. Conduct an initial system performance test described in section 8.1.3 as well before the test to validate the sampling components and procedures before sampling. After the test commences, a system performance check is required after each run. You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999.

11.0 Analytical Procedure

Because sample collection and analysis are performed together (see section 8.0), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

ACE = Analyzer calibration error, percent of calibration span.

CD = Calibration drift, percent.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{H2S} = Concentration of the system performance check gas, ppmv H_2S.

C_S = Measured concentration of the system performance gas when introduced in system calibration mode, ppmv H_2S.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv SO_2.

C_{SO2} = Unadjusted sample SO_2 concentration, ppmv.

C_{TRS} = Total reduced sulfur concentration corrected for system performance, ppmv.

CS = Calibration span, ppmv.

DF = Dilution system (if used) dilution factor, dimensionless.

SP = System performance, percent.

12.2 Analyzer Calibration Error. For non-dilution systems, use Equation 16C–1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_v}{CS} X\,100 \qquad \text{Eq. 16C-1}$$

12.3 System Performance Check. Use Equation 16C–2 to calculate the system performance.

$$SP = \frac{C_S - C_{H2S}}{C_{H2S}} x\,100 \qquad \text{Eq. 16C-2}$$

12.4 Calibration Drift. Use Equation 16C–3 to calculate the calibration drift at a single concentration level after a run or series of runs (not to exceed a 24-hr period) from initial calibration. Compare the single-level calibration gas error (ACE_n) to the original error obtained for that gas in the initial analyzer calibration error test (ACE_i).

$$CD = \left| ACE_i - ACE_n \right| \qquad \text{Eq. 16C-3}$$

12.5 TRS Concentration as SO_2. For each sample or test run, calculate the arithmetic average of SO_2 concentration values (e.g., 1-minute averages). Then calculate the sample TRS concentration by adjusting the average value of C_{SO2} for system performance using Equation 16C–4.

$$C_{TRS} = \frac{\overline{C_{SO2}}}{1 - \left|\overline{SP}\right|} \qquad \text{Eq. 16C-4}$$

13.0 Method Performance

13.1 Analyzer Calibration Error. At each calibration gas level (low, mid, and high), the calibration error must either not exceed 5.0 percent of the calibration gas concentration or $|C_{Dir} - C_v|$ must be ≤0.5 ppmv.

13.2 System Performance. Each system performance check must not deviate from the system performance gas concentration by more than 20 percent. Alternatively, the results are acceptable if $|C_s - C_{H2S}|$ is ≤0.5 ppmv.

13.3 Calibration Drift. The calibration drift at the end of any run or series of runs within a 24-hour period must not differ by more than 3.0 percent from the original ACE at the test concentration level or $|ACEi - ACE_n|$ must not exceed 0.5 ppmv.

13.4 Interference Check. For the analyzer, the total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.5 percent of the calibration span. Any interference is also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span <5 ppmv.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. The references are the same as in section 16.0 of Method 16, section 17.0 of Method 16A, and section 17.0 of Method 6C.
2. National Council of the Paper Industry for Air and Stream Improvement, Inc,. A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.
3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

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

METHOD 17—DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

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 have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

NOTE: Particulate matter is not an absolute quantity. It is a function of temperature and pressure. Therefore, to prevent variability in PM emission regulations and/or associated test methods, the temperature and pressure at which PM is to be measured must be carefully defined. Of the two variables (*i.e.*, temperature and pressure), temperature has the greater effect upon the amount of PM in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible. In Method 5, 120 °C (248 °F) is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standard, PM is defined with respect to temperature. In order to maintain a collection temperature of 120 °C (248 °F), Method 5 employs a heated glass sample probe and a heated filter holder. This equipment is somewhat cumbersome and requires care in its operation. Therefore, where PM concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass probe and the heating systems, and to sample at stack temperature.

1.2 Applicability. This method is applicable for the determination of PM emissions, where PM concentrations are known to be independent of temperature over the normal range of temperatures characteristic of emissions from a specified source category. It is intended to be used only when specified by an applicable subpart of the standards, and only within the applicable temperature limits (if specified), or when otherwise approved by the Administrator. This method is not applicable to stacks that contain liquid droplets or are saturated with water vapor. In addition, this method shall not be used as written if the projected cross-sectional area of the probe extension-filter holder assembly covers more than 5 percent of the stack cross-sectional area (see section 8.1.2).

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 Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at stack temperature. The PM mass is determined gravimetrically after the removal of uncombined water.

3.0 Definitions

Same as Method 5, 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.

6.0 Equipment and Supplies

6.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17–1. The sampling train components and operation and maintenance are very similar to Method 5, which should be consulted for details.

6.1.1 Probe Nozzle, Differential Pressure Gauge, Metering System, Barometer, Gas Density Determination Equipment. Same as in Method 5, sections 6.1.1, 6.1.4, 6.1.8, 6.1.9, and 6.1.10, respectively.

6.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or quartz glass, or stainless steel. If a gasket is used, it shall be made of silicone rubber, Teflon, or stainless steel. Other holder and gasket materials may be used, subject to the approval of the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

6.1.3 Probe Extension. Any suitable rigid probe extension may be used after the filter holder.

6.1.4 Pitot Tube. Same as in Method 5, section 6.1.3.

6.1.4.1 It is recommended (1) that the pitot tube have a known baseline coefficient, determined as outlined in section 10 of Method 2; and (2) that this known coefficient be preserved by placing the pitot tube in an interference-free arrangement with respect to the sampling nozzle, filter holder, and temperature sensor (see Figure 17–1). Note that the 1.9 cm (¾-in.) free-space between the nozzle and pitot tube shown in Figure 17–1, is based on a 1.3 cm (½-in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the free-space shall be 1.9 cm (¾-in.) with the largest sized nozzle in place.

6.1.4.2 Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17–1 (or the equivalent of these requirements, *e.g.*, Figure 2–4 of Method 2) may be used; however, the pitot tube coefficients of such assemblies shall be determined by calibration, using methods subject to the approval of the Administrator.

6.1.5 Condenser. It is recommended that the impinger system or alternatives described in Method 5 be used to determine the moisture content of the stack gas. Flexible tubing may be used between the probe extension and condenser. Long tubing lengths may affect the moisture determination.

6.2 Sample Recovery. Probe-liner and probe-nozzle brushes, wash bottles, glass sample storage containers, petri dishes, graduated cylinder and/or balance, plastic storage containers, funnel and rubber policeman, funnel. Same as in Method 5, sections 6.2.1 through 6.2.8, respectively.

6.3 Sample Analysis. Glass weighing dishes, desiccator, analytical balance, balance, beakers, hygrometer, temperature sensor. Same as in Method 5, sections 6.3.1 through 6.3.7, respectively.

7.0 Reagents and Standards

7.1 Sampling. Filters, silica gel, water, crushed ice, stopcock grease. Same as in Method 5, sections 7.1.1, 7.1.2, 7.1.3, 7.1.4, and 7.1.5, respectively. Thimble glass fiber filters may also be used.

7.2 Sample Recovery. Acetone (reagent grade). Same as in Method 5, section 7.2.

7.3 Sample Analysis. Acetone and Desiccant. Same as in Method 5, sections 7.3.1 and 7.3.2, respectively.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling.

8.1.1 Pretest Preparation. Same as in Method 5, section 8.1.1.

8.1.2 Preliminary Determinations. Same as in Method 5, section 8.1.2, except as follows: Make a projected-area model of the probe extension-filter holder assembly, with the pitot tube face openings positioned along the centerline of the stack, as shown in Figure 17–2. Calculate the estimated cross-section blockage, as shown in Figure 17–2. If the blockage exceeds 5 percent of the duct cross sectional area, the tester has the following options exist: (1) a suitable out-of-stack filtration method may be used instead of in-stack filtration; or (2) a special in-stack arrangement, in which the sampling and velocity measurement sites are separate, may be used; for details concerning this approach, consult with the Administrator (see also Reference 1 in section 17.0). Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

8.1.3 Preparation of Sampling Train. Same as in Method 5, section 8.1.3, except the following: Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as in Figure 17–1, using a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers.

8.1.4 Leak-Check Procedures. Same as in Method 5, section 8.1.4, except that the filter holder is inserted into the stack during the sampling train leak-check. To do this, plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature. Insert the filter holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream.

8.1.5 Sampling Train Operation. The operation is the same as in Method 5. Use a data sheet such as the one shown in Figure 5–3 of Method 5, except that the filter holder temperature is not recorded.

8.1.6 Calculation of Percent Isokinetic. Same as in Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Proper cleanup procedure begins as soon as the probe extension assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

8.2.2 When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, forcing condenser water backward.

8.2.3 Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger (or condenser) and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. Disconnect the probe extension from the condenser; cap the probe extension outlet. After wiping off the silicone grease, cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

8.2.4 Transfer both the filter holder-probe nozzle assembly and the condenser to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.2.5 Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone from the wash bottle being used and place it in a glass sample container labeled ‘‘acetone blank.’’ Inspect the train prior to and during disassembly and not any abnormal conditions. Treat the sample as discussed in Method 5, section 8.2.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

The calibrations of the probe nozzle, pitot tube, metering system, temperature sensors, and barometer are the same as in Method 5, sections 10.1 through 10.3, 10.5, and 10.6, respectively.

11.0 Analytical Procedure

Same as in Method 5, section 11.0. Analytical data should be recorded on a form similar to that shown in Figure 5–6 of Method 5.

12.0 Data Analysis and Calculations.

Same as in Method 5, section 12.0.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Same as in Method 5, section 16.0.

17.0 References

Same as in Method 5, section 17.0, with the addition of the following:

1. Vollaro, R.F. Recommended Procedure for Sample Traverses in Ducts Smaller than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

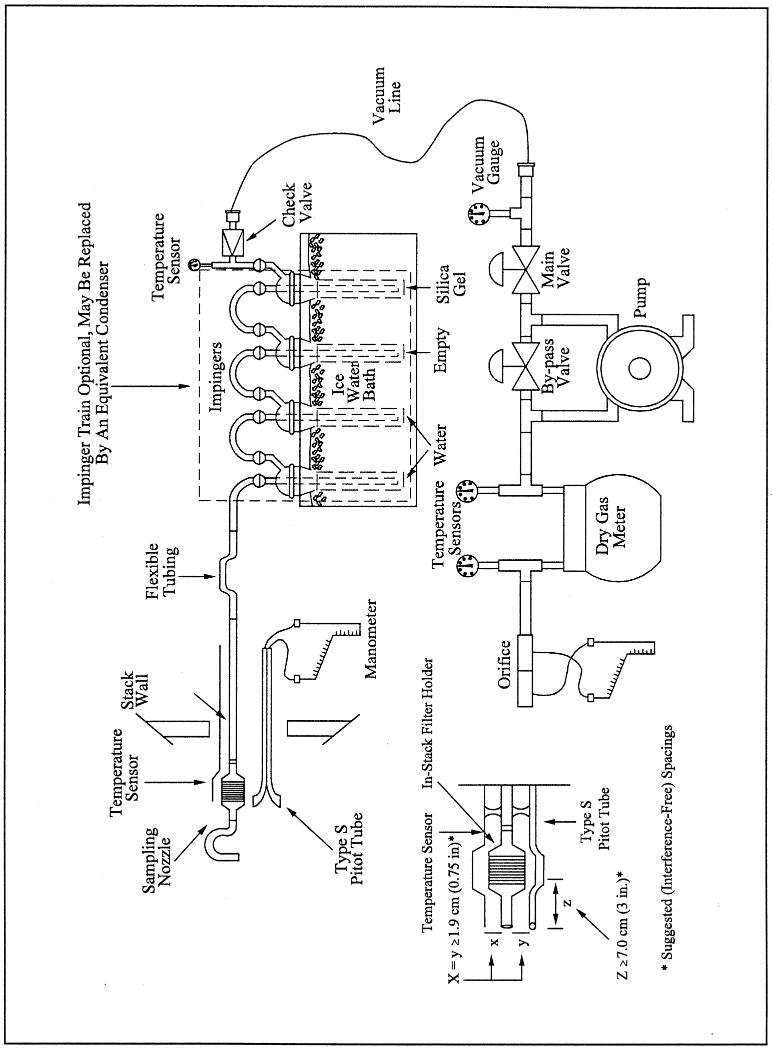

Figure 17-1. Particulate Matter Sampling Train with In-Stack Filter.

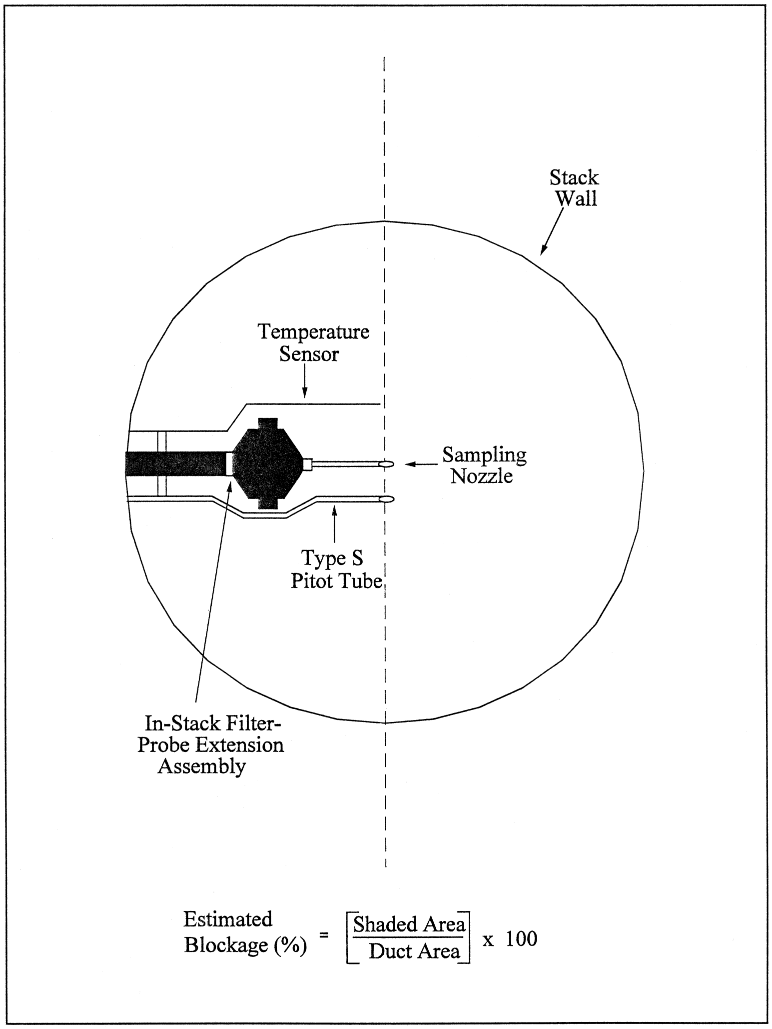

Figure 17-2. Projected-Area Model of Cross-Section Blockage (approximate average for a sample traverse) Caused by an In-Stack Filter Holder-Probe Extension Assembly.

METHOD 18—MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

NOTE: This method is not inclusive with respect to 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 have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

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

1.0 Scope and Application

1.1 Analyte. Total gaseous organic compounds.

1.2 Applicability.

1.2.1 This method is designed to measure gaseous organics emitted from an industrial source. While designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, *e.g.*, ECD, ELCD, and helium ionization detectors. Some other types of detectors are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.

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

1.3 Range. The lower range of this method is determined by the sampling system; adsorbents may be used to concentrate the sample, thus lowering the limit of detection below the 1 part per million (ppm) typically achievable with direct interface or bag sampling. The upper limit is governed by GC detector saturation or column overloading; the upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be governed by condensation of higher boiling compounds.

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

2.0 Summary of Method

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

3.0 Definitions [Reserved]

4.0 Interferences

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

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

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

4.4 To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover).

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.

6.0 Equipment and Supplies

6.1 Equipment needed for the presurvey sampling procedure can be found in section 16.1.1.

6.2 Equipment needed for the integrated bag sampling and analysis procedure can be found in section 8.2.1.1.1.

6.3 Equipment needed for direct interface sampling and analysis can be found in section 8.2.2.1.

6.4 Equipment needed for the dilution interface sampling and analysis can be found in section 8.2.3.1.

6.5 Equipment needed for adsorbent tube sampling and analysis can be found in section 8.2.4.1.

7.0 Reagents and Standards

7.1 Reagents needed for the presurvey sampling procedure can be found in section 16.1.2.

8.0 Sample Collection, Preservation, Storage, and Transport

8.2 Final Sampling and Analysis Procedure. Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 8.2.1, 8.2.2, 8.2.3 or 8.2.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

8.2.1 Integrated Bag Sampling and Analysis.

8.2.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Use a field sample data sheet as shown in Figure 18–10. Collect triplicate samples from each sample location.

8.2.1.1.1 Apparatus.

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

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

8.2.1.1.1.3 Needle Valve. To control gas flow.

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

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

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

8.2.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18–9. Leak-check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack or at a point no closer to the walls than 1 in., and start the pump. Set the flow rate so that the final volume of the sample is approximately 80 percent of the bag capacity. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18–10. Protect the bag and its container from sunlight. Record the time lapsed between sample collection and analysis, and then conduct the recovery procedure in Section 8.4.2.

8.2.1.2 Direct Pump Sampling Procedure. Follow 8.2.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of inert material not affected by the stack gas. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

8.2.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 8.2.1.1 except replace the pump with another evacuated can (see Figure 18–9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

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

8.2.1.4.1 First Alternative Procedure. Heat the box containing the sample bag to 120 °C (±5 °C). Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to 120 °C (±5 °C) until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

8.2.1.4.2 Second Alternative Procedure. Prefill the bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 10.1.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors before sampling each bag through dilution and analysis of gases of known concentration.

8.2.1.5 Analysis of Bag Samples.

8.2.1.5.1 Apparatus. Same as section 8.1. A minimum of three gas standards are required.

8.2.1.5.2 Procedure.

8.2.1.5.2.1 Establish proper GC operating conditions as described in section 10.2, and record all data listed in Figure 18–7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with calibration gas mixture, and activate the valve (sample pressure at the inlet to the GC introduction valve should be similar during calibration as during actual sample analysis). Obtain at least three chromatograms for the mixture. The results are acceptable when the peak areas for the three injections agree to within 5 percent of their average. If they do not agree, run additional samples or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in section 10.2.

8.2.1.5.2.2 Analyze the three source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Analyze each bag sample three times. Record the data in Figure 18–11. If certain items do not apply, use the notation ''N.A.'' If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4. After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. Compare the average response factor of the pre- and post-test analysis for each compound. If they differ by >5percent, analyze the other calibration gas levels for that compound, and prepare a calibration curve using all the pre- and post-test calibration gas mixture values. If the two response factor averages (pre-and post-test) differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values.

8.2.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in section 8.2.1.4, determine the stack gas water content by Method 4.

8.2.1.8 Emission Calculations. From the calibration curve described in section 8.2.1.5, select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample using Equation 18–5 in section 12.6.

8.2.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration falls within the linear range of the detector. Adhere to all safety requirements with this method.

8.2.2.1 Apparatus.

8.2.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as dictated by duct temperature and reactivity of target compounds. A filter or glass wool plug may be needed if particulate is present in the stack gas. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining a temperature greater than 110 °C.

8.2.2.1.2 Sample Lines. 6.4-mm OD (or other diameter as needed) Teflon lines, heat-traced to prevent condensation of material (greater than 110 °C).

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

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

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

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

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

8.2.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

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

8.2.2.1.10 Gas Cylinders. Carrier gas, oxygen and fuel as needed to run GC and detector.

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

8.2.2.1.12 Recorder/Integrator. To record results.

8.2.2.2 Procedure. Calibrate the GC using the procedures in section 8.2.1.5.2.1. To obtain a stack gas sample, assemble the sampling system as shown in Figure 18–12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the target temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature greater than 110 °C. Conduct a 3-point calibration of the GC by analyzing each gas mixture in triplicate. Generate a calibration curve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the stack gas sample using the same conditions as for the calibration gas mixture. For each run, sample, analyze, and record five consecutive samples. A test consists of three runs (five samples per run times three runs, for a total of fifteen samples). After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. For each calibration standard, compare the pre- and post-test average response factors (RF) for each compound. If the two calibration RF values (pre- and post-analysis) differ by more than 5 percent from their mean value, then analyze the other calibration gas levels for that compound and determine the stack gas sample concentrations by comparison to both calibration curves (this is done by preparing a calibration curve using all the pre- and post-test calibration gas mixture values.) If the two calibration RF values differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values. Record this calibration data and the other required data on the data sheet shown in Figure 18–11, deleting the dilution gas information.

NOTE: Take care to draw all samples and calibration mixtures through the sample loop at the same pressure.

8.2.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

8.2.2.5 Emission Calculations. Same as section 8.2.1.8.

8.2.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the section 8.2.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

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

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

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

8.2.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to Teflon tubing.

8.2.3.1.4 Flowmeters. Two, for measurement of diluent gas.

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

8.2.3.1.6 Heated Box. Suitable for being heated to 120 °C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18–13. The heated box shown in Figure 18–13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

NOTE: Care must be taken to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.

8.2.3.2 Procedure.

8.2.3.2.1 Assemble the apparatus by connecting the heated box, shown in Figure 18–13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3 °C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds (greater than 110 °C). Calibrate the GC through the dilution system by following the procedures in section 8.2.1.5.2.1. Determine the concentration of the diluted calibration gas using the dilution factor and the certified concentration of the calibration gas. Record the pertinent data on the data sheet shown in Figure 18–11.

8.2.3.2.2 Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards.

8.2.3.2.3 Analyze the audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

8.2.3.3 Determination of Stack Gas Moisture Content. Same as section 8.2.2.3.

8.2.3.4 Quality Assurance. Same as section 8.2.2.4.

8.2.3.5 Emission Calculations. Same as section 8.2.2.5, with the dilution factor applied.

8.2.4 Adsorption Tube Procedure. Any commercially available adsorbent is allowed for the purposes of this method, as long as the recovery study criteria in section 8.4.3 are met. Help in choosing the adsorbent may be found by calling the distributor, or the tester may refer to National Institute for Occupational Safety and Health (NIOSH) methods for the particular organics to be sampled. For some adsorbents, the principal interferent will be water vapor. If water vapor is thought to be a problem, the tester may place a midget impinger in an ice bath before the adsorbent tubes. If this option is chosen, the water catch in the midget impinger shall be analyzed for the target compounds. Also, the spike for the recovery study (in section 8.4.3) shall be conducted in both the midget impinger and the adsorbent tubes. The combined recovery (add the recovered amount in the impinger and the adsorbent tubes to calculate R) shall then meet the criteria in section 8.4.3.

NOTE: Post-test leak-checks are not allowed for this technique since this can result in sample contamination.

8.2.4.1 Additional Apparatus. The following items (or equivalent) are suggested.

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

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

8.2.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices.

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

8.2.4.1.5 Stopwatch. To time sampling and pump rate calibration.

8.2.4.1.6 Adsorption Tubes. Precleaned adsorbent, with mass of adsorbent to be determined by calculating breakthrough volume and expected concentration in the stack.

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

8.2.4.1.8 Rotameter. O to 100 cc/min, to detect changes in flow rate during sampling.

8.2.4.2 Sampling and Analysis.

8.2.4.2.1 Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

8.2.4.2.2 Use a sample probe, if required, to obtain the sample at the centroid of the duct or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Adsorption tubes should be maintained vertically during the test in order to prevent channeling. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Calibrate the instrument and then analyze the emission samples.

8.2.4.3 Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses using the procedures in section 8.2.1.5.2.1.

8.2.4.4 Quality Assurance.

8.2.4.4.1 Determine the recovery efficiency of the pollutants of interest according to section 8.4.3.

8.2.4.4.2 Determination of Sample Collection Efficiency (Optional). If sample breakthrough is thought to be a problem, a routine procedure for determining breakthrough is to analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and back-up), it is usually a sign of sample breakthrough. For the purposes of this method, only the recovery efficiency value (Section 8.4.3) is used to determine the appropriateness of the sampling and analytical procedure.

8.2.4.4.3 Volume Flow Rate Checks. Perform this check immediately after sampling with all sampling train components in place.

Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and record the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

8.2.4.4.4 Calculations. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results according to the applicable procedure in section 8.4.3. Report results as ppm by volume, dry basis.

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

8.4 Recovery Study. After conducting the presurvey and identifying all of the pollutants of interest, conduct the appropriate recovery study during the test based on the sampling system chosen for the compounds of interest.

8.4.1 Recovery Study for Direct Interface or Dilution Interface Sampling. If the procedures in section 8.2.2 or 8.2.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in section 8.2.2.2 or 8.2.3.2, as appropriate. Upon successful completion of the appropriate calibration procedure, attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter. Repeat the calibration procedure by sampling and analyzing the mid-level calibration gas through the entire sampling and analytical system in triplicate. The mean of the calibration gas response sampled through the probe shall be within 10 percent of the analyzer response. If the difference in the two means is greater than 10 percent, check for leaks throughout the sampling system and repeat the analysis of the standard through the sampling system until this criterion is met.

8.4.2 Recovery Study for Bag Sampling.

8.4.2.1 Follow the procedures for the bag sampling and analysis in section 8.2.1. After analyzing all three bag samples, choose one of the bag samples and tag this bag as the spiked bag. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all of the target pollutants. The theoretical concentration, in ppm, of each spiked compound in the bag shall be 40 to 60 percent of the average concentration measured in the three bag samples. If a target compound was not detected in the bag samples, the concentration of that compound to be spiked shall be 5 times the limit of detection for that compound. Store the spiked bag for the same period of time as the bag samples collected in the field. After the appropriate storage time has passed, analyze the spiked bag three times. Calculate the average fraction recovered (R) of each spiked target compound with the equation in section 12.7.

8.4.2.2 For the bag sampling technique to be considered valid for a compound, $0.70 \leq R \leq 1.30$. If the R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

8.4.3 Recovery Study for Adsorption Tube Sampling. If following the adsorption tube procedure in section 8.2.4, conduct a recovery study of the compounds of interest during the actual field test. Set up two identical sampling trains. Collocate the two sampling probes in the stack. The probes shall be placed in the same horizontal plane, where the first probe tip is 2.5 cm from the outside edge of the other. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike all of the compounds of interest (in gaseous or liquid form) onto the adsorbent tube(s) in the spiked train before sampling. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be collected with the unspiked train. Sample the stack gas into the two trains simultaneously. Analyze the adsorbents from the two trains utilizing identical analytical procedures and instrumentation. Determine the fraction of spiked compound recovered (R) using the equations in section 12.9.

8.4.3.1 Repeat the procedure in section 8.4.3 twice more, for a total of three runs. In order for the adsorbent tube sampling and analytical procedure to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is the average of three runs). If the average R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in section 12.8.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures

Section	Quality control measure	Effect
8.4.1	Recovery study for direct interface or dilution interface sampling.	Ensure that there are no significant leaks in the sampling system.
8.4.2	Recovery study for bag sampling	Demonstrate that proper sampling/analysis procedures were selected.
8.4.3	Recovery study for adsorption tube sampling.	Demonstrate that proper sampling/analysis procedures were selected.

10.0 Calibration and Standardization.

10.1 Calibration Standards. Obtain calibration gas standards for each target compound to be analyzed. Commercial cylinder gases certified by the manufacturer to be accurate to within 1 percent of the certified label value are preferable, although cylinder gases certified by the manufacturer to 2 percent accuracy are allowed. Another option allowed by this method is for the tester to obtain high concentration certified cylinder gases and then use a dilution system meeting the requirements of Test Method 205, 40 CFR Part 51, Appendix M to make multi-level calibration gas standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If samples are collected in adsorbent tubes and extracted using solvent extraction, prepare or obtain standards in the same solvent used for the sample extraction procedure. Verify the stability of all standards for the time periods they are used.

10.2 Preparation of Calibration Curves.

10.2.1 Establish proper GC conditions, then flush the sampling loop for 30 seconds. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Analyze each standard in triplicate.

10.2.2 Repeat this procedure for each standard. Prepare a graphical plot of concentration (C_s) versus the calibration area values. Perform a regression analysis, and draw the least square line.

11.0 Analytical Procedures

11.1 Analysis Development

11.1.1 Selection of GC Parameters

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

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

11.1.1.2 Preliminary GC Adjustment. Using the standards and column obtained in section 11.1.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

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

11.1.1.4 Presurvey Sample Analysis.

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

11.1.1.4.2 Use the GC conditions determined by the procedure of section 11.1.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

11.1.1.4.3 If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 10.2) to obtain an estimate of the concentrations.

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

12.0 Data Analysis and Calculations

12.1 Nomenclature.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.
C_s = Concentration of the organic from the calibration curve, ppm.
G_v = Gas volume or organic compound injected, ml.
L_v = Liquid volume of organic injected, µl.
M = Molecular weight of organic, g/g-mole.
m_s = Total mass of compound measured on adsorbent with spiked train (µg).
m_u = Total mass of compound measured on adsorbent with unspiked train (µg).
m_v = Mass per volume of spiked compound measured (µg/L).
P_i = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.
P_m = Absolute pressure of dry gas meter, mm Hg.
P_r = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.
P_s = Absolute pressure of syringe before injection, mm Hg.
q_c = Flow rate of the calibration gas to be diluted.
q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.
q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.
q_d = Diluent gas flow rate.
q_{d1} = Flow rate of diluent gas in stage 1.
q_{d2} = Flow rate of diluent gas in stage 2.
s = Theoretical concentration (ppm) of spiked target compound in the bag.
S = Theoretical mass of compound spiked onto adsorbent in spiked train (µg).
t = Measured average concentration (ppm) of target compound and source sample (analysis results subsequent to bag spiking)
T_i = Sample loop temperature at the time of sample analysis, °K.
T_m = Absolute temperature of dry gas meter, °K.
T_s = Absolute temperature of syringe before injection, °K.
u = Source sample average concentration (ppm) of target compound in the bag (analysis results before bag spiking).
V_m = Gas volume indicated by dry gas meter, liters.
v_s = volume of stack gas sampled with spiked train (L).
v_u = volume of stack gas sampled with unspiked train (L).
X = Mole or volume fraction of the organic in the calibration gas to be diluted.
Y = Dry gas meter calibration factor, dimensionless.
µl = Liquid organic density as determined, g/ml.
24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.
1000 = Conversion factor, ml/liter.
10^6 = Conversion to ppm.

12.2 Calculate the concentration, C_s, in ppm using the following equation:

$$C_s = \frac{10^6\left(\overline{X}q_c\right)}{q_c + q_d} \qquad \text{Eq. 18-1}$$

12.3 Calculate the concentration, C_s, in ppm of the organic in the final gas mixture using the following equation:

$$C_s = 10^6\,\overline{X}\left(\frac{q_{c1}}{q_{c1}+q_{d1}}\right)\left(\frac{q_{c2}}{q_{c2}+q_{d2}}\right) \qquad \text{Eq. 18-2}$$

12.4 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{G_v \times 10^6 \frac{293}{T_s} \frac{P_s}{760}}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} \qquad \text{Eq. 18-3}$$

$$= \frac{G_v \times 10^3 \frac{P_s}{T_s} \frac{T_m}{P_m}}{V_m Y}$$

12.5 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{\frac{L_v}{M} \rho \left(24.055 \times 10^6\right)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \rho T_m}{M V_m Y P_m} \qquad \text{Eq. 18-4}$$

12.6 Calculate the concentration, C_c, in ppm, dry basis, of each organic is the sample using the following equation:

$$C_c = \frac{C_s P_r T_i F_r}{P_i T_r \left(1 - B_{ws}\right)} \qquad \text{Eq. 18-5}$$

12.7 Calculate the average fraction recovered (R) of each spiked target compound using the following equation:

$$R = \frac{t - u}{s} \qquad \text{Eq. 18-6}$$

12.8 Correct all field measurements with the calculated R value for that compound using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Concentration (ppm)}}{R} \qquad \text{Eq. 18-7}$$

12.9 Determine the mass per volume of spiked compound measured using the following equation:

$$m_v = \frac{m_s}{V_s} - \frac{m_u}{V_u} \qquad \text{Eq. 18-8}$$

12.10 Calculate the fraction of spiked compound recovered, R, using the following equation:

$$R = \frac{m_v \times v_s}{S} \qquad \text{Eq. 18-9}$$

13.0 Method Performance

13.1 Since a potential sample may contain a variety of compounds from various sources, a specific precision limit for the analysis of field samples is impractical. Precision in the range of 5 to 10 percent relative standard deviation (RSD) is typical for gas chromatographic techniques, but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Triplicate analyses of calibration standards fall within 5 percent of their mean value.

(c) Recovery. After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in section 8.4. Conduct the appropriate recovery study in section 8.4 at each sampling point where the method is being applied. Submit the data and results of the recovery procedure with the reporting of results under section 8.3.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Optional Presurvey and Presurvey Sampling.

NOTE: Presurvey screening is optional. Presurvey sampling should be conducted for sources where the target pollutants are not known from previous tests and/or process knowledge.

Perform a presurvey for each source to be tested. Refer to Figure 18–1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

16.1.1 Apparatus. This apparatus list also applies to sections 8.2 and 11.

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

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

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

16.1.1.4 Flow Meter. To measure flow rates.

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

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

16.1.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing calibration standards. Other appropriate sizes can be used.

16.1.1.8 Tubing Fittings. To plumb GC and gas cylinders.

16.1.1.9 Septa. For syringe injections.

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

16.1.1.11 Soap Film Flowmeter. To determine flow rates.

16.1.1.12 Flexible Bags. Tedlar or equivalent, 10- and 50-liter capacity, for preparation of standards. (Verify through the manufacturer that the Tedlar alternative is suitable for the compound of interest and make this verifying information available for inspection.)

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

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

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

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

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

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

16.1.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

16.1.1.20 Barometer. To measure barometric pressure.

16.1.2 Reagents.

16.1.2.1 Water. Deionized distilled.

16.1.2.2 Methylene chloride.

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

16.1.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

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

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

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

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

16.1.3 Sampling.

16.1.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples may be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene chloride (or other non-target pollutant solvent, or heat and humidified air). Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace, and apply heat up to 500 °C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Return the stopcocks to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape. Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

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

16.1.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in section 8.3.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close off the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

16.1.3.2 Flexible Bag Procedure. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, can be used to obtain the pre-survey sample. Use new bags, and leak-check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak-check and sample collection procedures given in Section 8.2.1.

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

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

16.1.5 Collection of Presurvey Samples with Adsorption Tube. Follow section 8.2.4 for presurvey sampling.

17.0 References

1. American Society for Testing and Materials. C1 Through C5 Hydrocarbons in the Atmosphere by Gas Chromatography. ASTM D 2820–72, Part 23. Philadelphia, Pa. 23:950–958. 1973.

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18.0 Tables, Diagrams, Flowcharts, and Validation Data

I. Name of company ______
Date ______
Address ______
______
Contracts ______
Phone ______
Process to be sampled ______
______
______
Duct or vent to be sampled ______
______
II. Process description ______
______
______
______
______
Raw material ______
______
______
Products ______
______
______
Operating cycle
Check: Batch ______ Continuous ______
Cyclic ______
Timing of batch or cycle ______
Best time to test ______
III. Sampling site ______
A. Description ______
Site decription ______
Duct shape and size ______

Material ______________________________
Wall thickness _______ inches
Upstream distance _______ inches _______ diameter
Downstream distance _______ inches _______ diameter
Size of port ______________________________
Size of access area ______________________
Hazards _______ Ambient temp. _______ °F

B. Properties of gas stream
Temperature _______ °C _______ °F, Data source _______
Velocity _______, Data source _______
Static pressure _______ inches H_2O, Data source _______
Moisture content _______%, Data source _______
Particulate content _______, Data source_______

Gaseous components
N_2 _______ % Hydrocarbons _______ ppm
O_2 _______% _______
CO _______ % _______ _______
CO_2 _______ % _______ _______
SO_2 _______ % _______ _______

Hydrocarbon components
_______ _______ ppm
_______ _______ ppm
_______ _______ ppm
_______ _______ ppm
_______ _______ ppm
_______ _______ ppm

C. Sampling considerations
Location to set up GC ____________________
____
Special hazards to be considered __________
____
Power available at duct __________________
Power available for GC __________________
Plant safety requirements ________________
____
Vehicle traffic rules _____________________
____
Plant entry requirements _________________
____
Security agreements ____________________
____
Potential problems _____________________
____

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

Figure 18–1. Preliminary Survey Data Sheet

Components to be analyzed and Expected concentration

____
____
____
____
____
____

Suggested chromatographic column _______
____
Column flow rate __ ml/min
Head pressure _______ mm Hg
Column temperature: Isothermal _______ °C, Programmed from _______ °C to _______ °C at _______ °C/min
Injection port/sample loop temperature _______ °C
Detector temperature _______ °C
Detector flow rates: Hydrogen _______ ml/min., head pressure _______ mm Hg, Air/Oxygen _______ ml/min., head pressure _______ mm Hg.
Chart speed _______ inches/minute
Compound data:
Compound and Retention time and Attenuation
____
____
____
____
____

Figure 18–2. Chromatographic Conditions Data Sheet

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE

	Standards		
	Mixture #1	Mixture #2	Mixture #3
Standards Preparation Data:			
Organic:			
Bag number or identification.			
Dry gas meter calibration factor.			
Final meter reading (liters).			
Initial meter reading (liters).			
Metered volume (liters).			
Average meter temperature (°K).			
Average meter pressure, gauge (mm Hg).			
Average atmospheric perssure (mm Hg).			
Average meter pressure, absolute (mm Hg).			
Syringe temperature (°K) (see section 10.1.2.1).			
Syringe pressure, absolute (mm Hg) (see section 10.1.2.1).			
Volume of gas in syringe (ml) (Section 10.1.2.1).			
Density of liquid organic (g/ml) (Section 10.1.2.1).			
Volume of liquid in syringe (ml) (Section 10.1.2.1).			

FIGURE 18–3. PREPARATION OF STANDARDS IN TEDLAR OR TEDLAR-EQULIVALENT BAGS AND CALIBRATION CURVE—Continued

	Standards		
	Mixture #1	Mixture #2	Mixture #3
GC Operating Conditions:			
Sample loop volume (ml).			
Sample loop temperature (°C).			
Carrier gas flow rate (ml/min).			
Column temperature:			
Initial (°C).			
Rate change (°C/min).			
Final (°C).			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24 hour clock).			
Distance to peak (cm).			
Chart speed (cm/min).			
Organic retention time (min).			
Attenuation factor.			
Peak height (mm).			
Peak area (mm$_2$).			
Peak area * attenuation factor (mm$_2$).			
Calculated concentration (ppm) (Equation 18–3 or 18–4).			

Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.

Flowmeter number or identification _______

Flowmeter Type ________________________

Method: Bubble meter___ Spirometer___

Wet test meter ___

Readings at laboratory conditions:

Laboratory temperature (T_{lab}) ___ °K

Laboratory barometric pressure (P_{lab})___ mm Hg

Flow data:

FLOWMETER

Reading (as marked)	Temp. (°K)	Pressure (absolute)

CALIBRATION DEVICE

Time (min)	Gas volume [a]	Flow rate [b]

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

[b] Convert to standard conditions (20 °C and 760 mm Hg). Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a ‘‘family’’ of calibration curves that cover the operating pressure and temperature ranges of the flowmeter. While the following technique should be verified before application, it may be possible to calculate flow rate reading for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (STD conditions)

Figure 18–4. Flowmeter Calibration

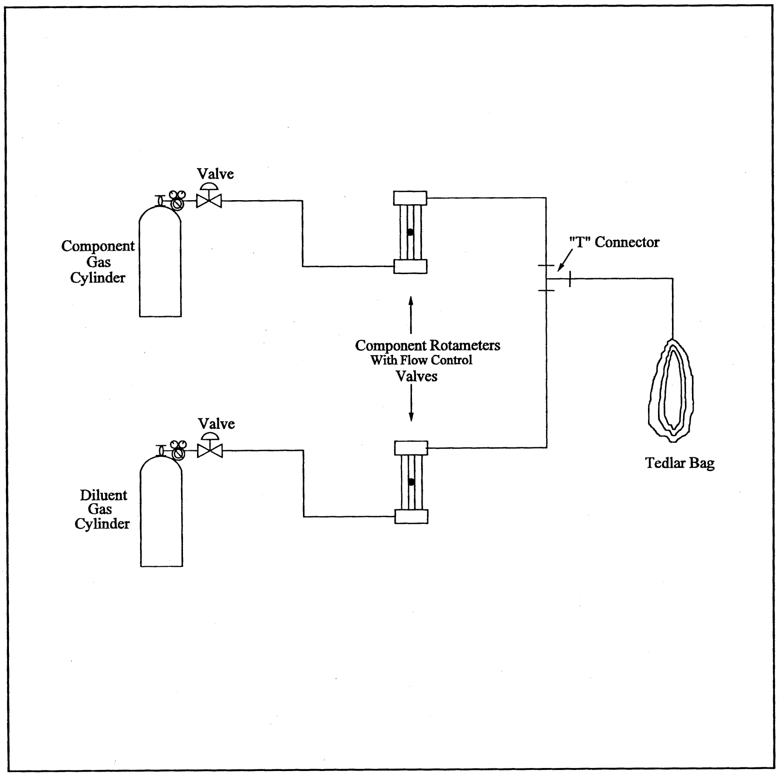


Figure 18-5. Single-Stage Calibration Gas Dilution System.

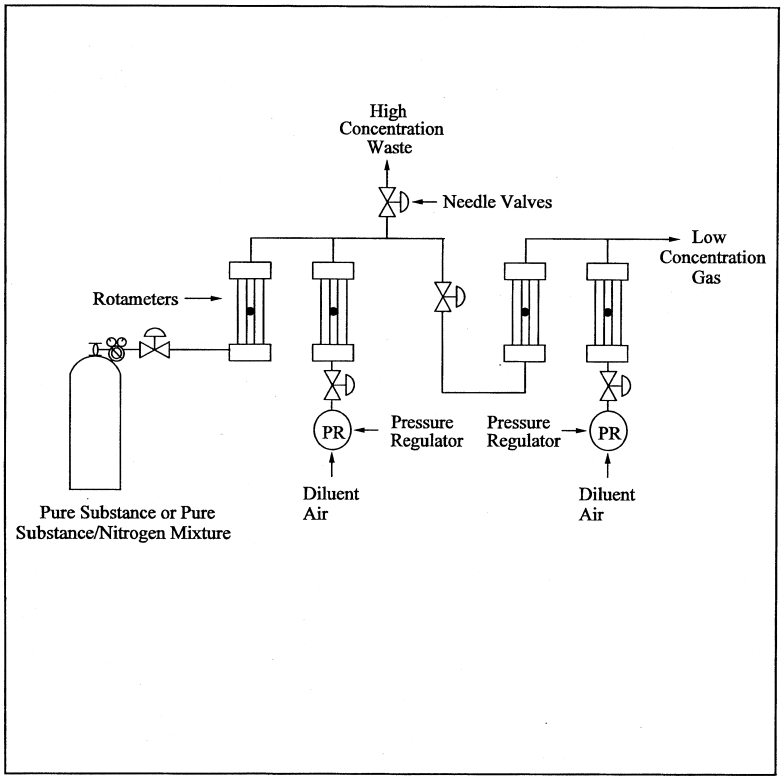


Figure 18-6. Two-Stage Dilution Apparatus.

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD

[Cylinder Standard: Organic ________ Certified Concentration ________ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Stage 1:			
Standard gas flowmeter reading.			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used):			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate Stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions			
Calculated concentration (ppm)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			

PREPARATION OF STANDARDS BY DILUTION OF CYLINDER STANDARD—Continued

[Cylinder Standard: Organic _______ Certified Concentration _______ ppm]

Standards preparation data:	Date:		
	Mixture 1	Mixture 2	Mixture 3
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area *attenuation factor			

Plot peak area *attenuation factor against calculated concentration to obtain calibration curve.

Figure 18–7. Standards Prepared by Dilution of Cylinder Standard

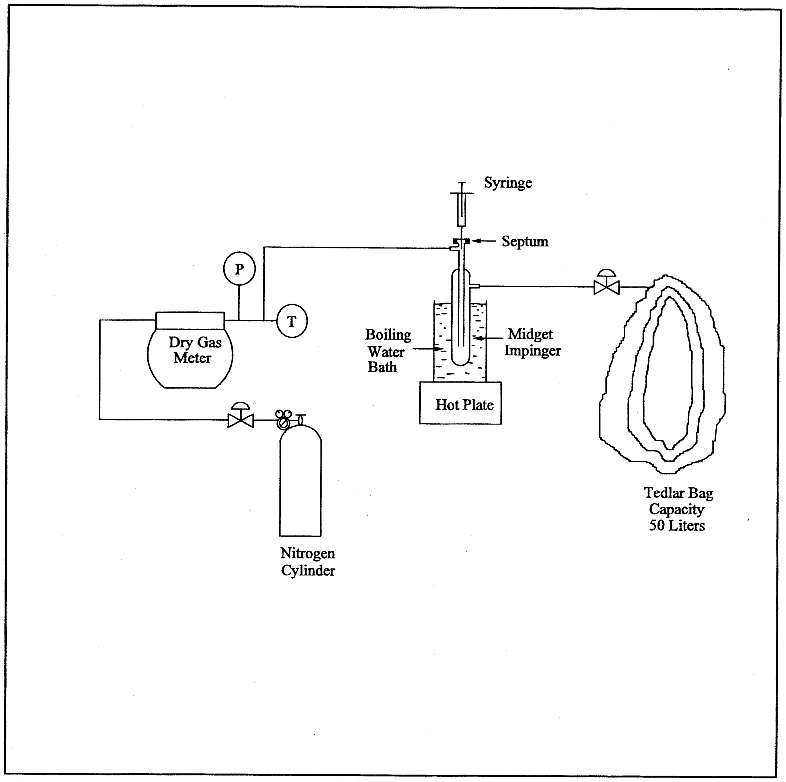


Figure 18-8. Apparatus for Preparation of Liquid Materials.

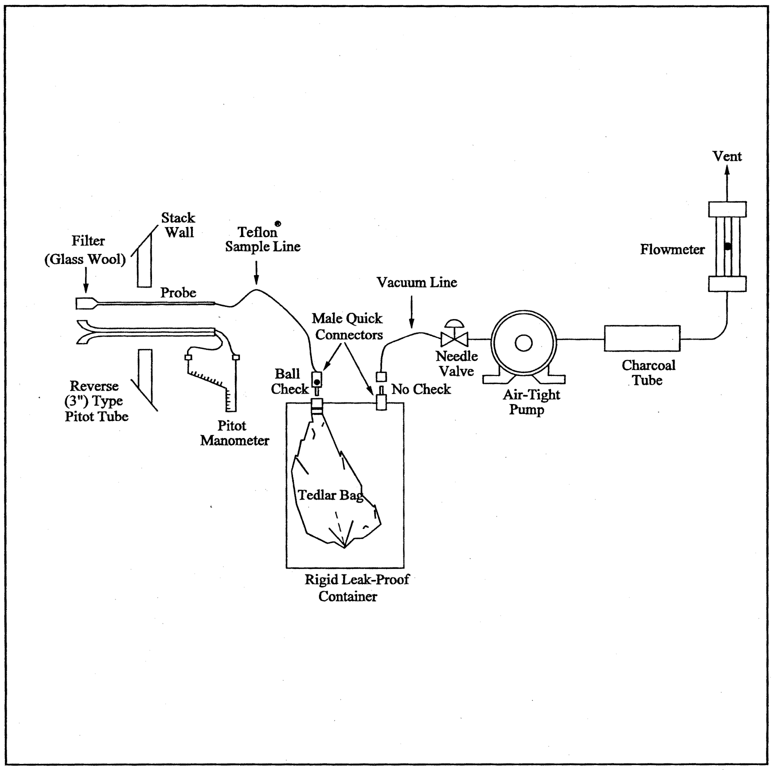


Figure 18-9. Integrated Bag Sampling Train.

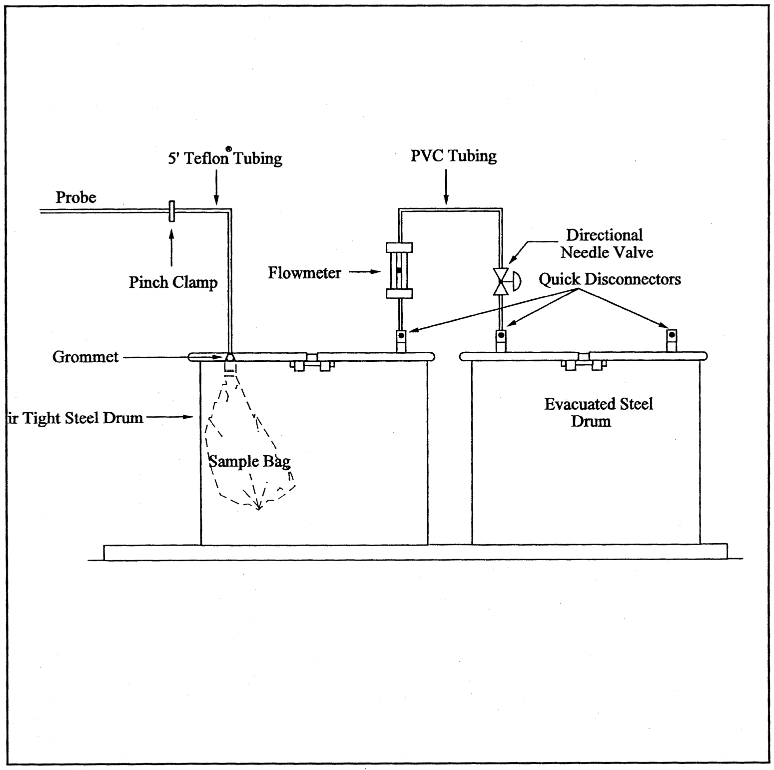


Figure 18-9a. Explosion Risk Gas Sampling Method.

PLANT________ DATE________ SITE________

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

Figure 18–10. Field Sample Data Sheet—Tedlar or Tedlar-Equivalent Bag Collection Method

PLANT ________________ DATE ______________ LOCATION ______________________

1. General information:
    - Source temperature (°C)
    - Probe temperature (°C)
    - Ambient temperature (°C)
    - Atmospheric pressure (mm)
    - Source pressure (″Hg)
    - Absolute source pressure (mm)
    - Sampling rate (liter/min)
    - Sample loop volume (ml)
    - Sample loop temperature (°C)
    - Columnar temperature:
        - Initial (°C) time (min)
        - Program rate (°C/min)
        - Final (°C)/time (min)
    - Carrier gas flow rate (ml/min)

PLANT _________________ DATE _______________ LOCATION ______________________—Continued

Detector temperature (°C) ....

Injection time (24-hour basis) ....

Chart Speed (mm/min) ....

Dilution gas flow rate (ml/min) ....

Dilution gas used (symbol) ....

Dilution ratio ....

2. FIELD ANALYSIS DATA—CALIBRATION GAS

2. [Run No. _______ Time __________]

Components	Area	Attenuation	A × A Factor	Conc.__ (ppm)

Figure 18–11. Field Analysis Data Sheets

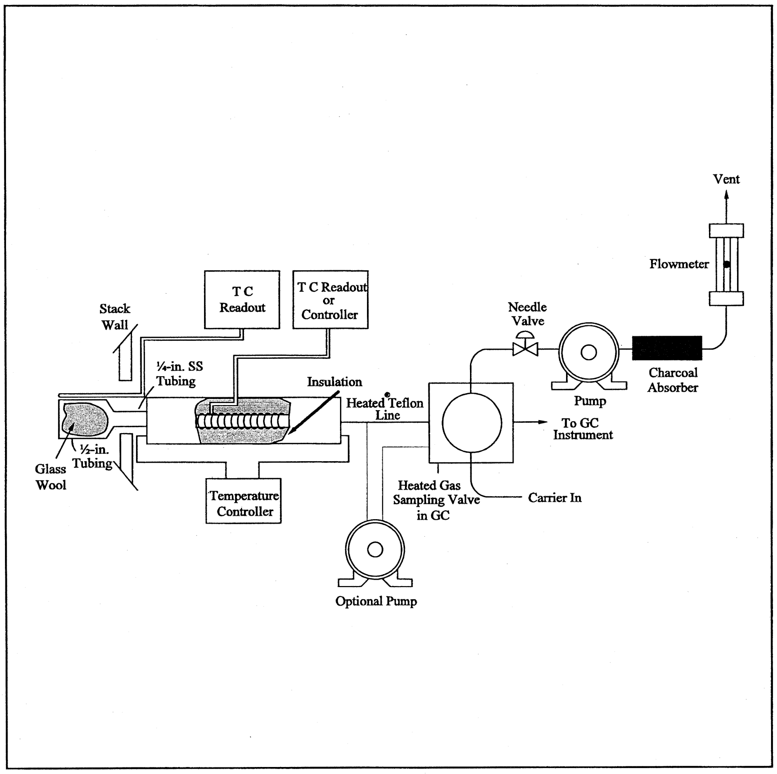


Figure 18-12. Direct Interface Sampling System.

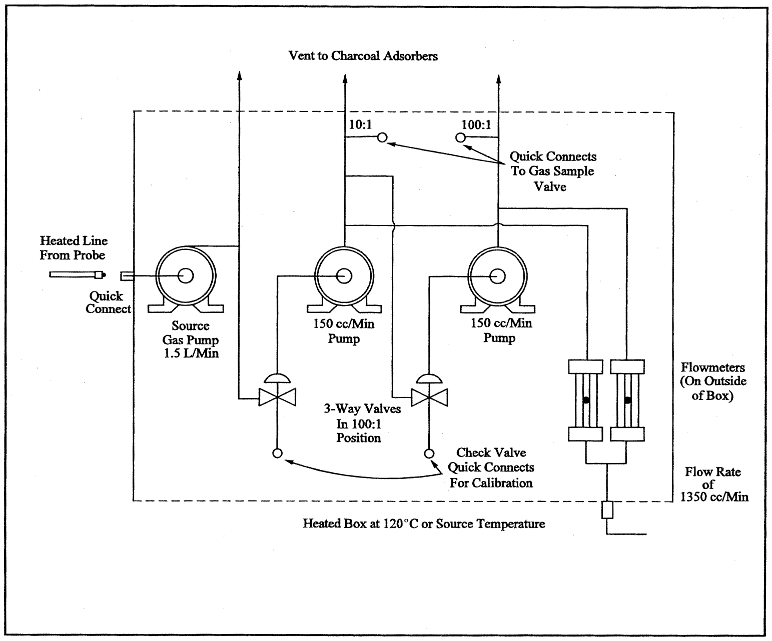


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

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

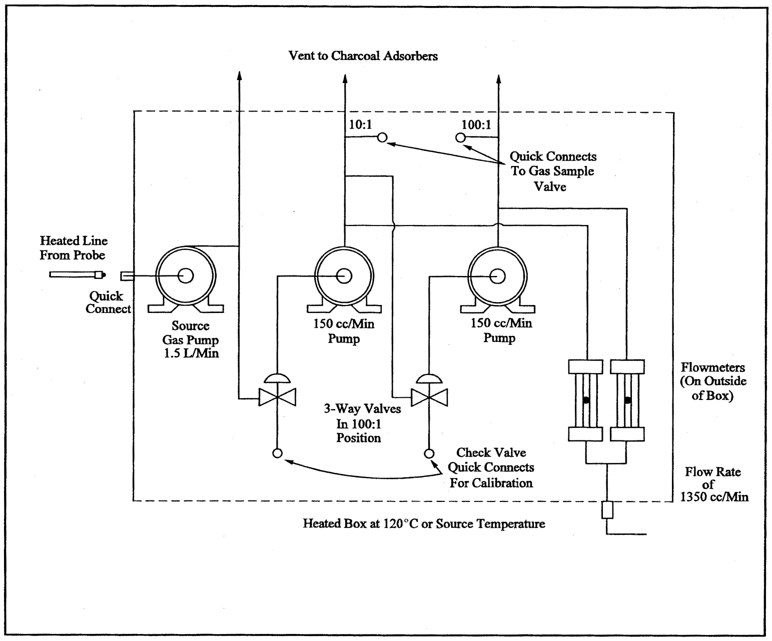


Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

[Respond with initials or number as appropriate]

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

Gaseous Organic Sampling and Analysis Data

Date ____________________

Location ____________________

Plant ____________________

GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST (RESPOND WITH INITIALS OR NUMBER AS APPROPRIATE)

1. Pre-survey data	Date
A. Grab sample collected	________
B. Grab sample analyzed for composition	________
Method GC	________
GC/MS	________
Other______________________	________
C. GC–FID analysis performed	________
2. Laboratory calibration curves prepared	________
A. Number of components	________
B. Number of concentrations per component (3 required)	________
C. OK obtained for field work	________
3. Sampling procedures.	
A. Method.	
Bag sample	________
Direct interface	________
Dilution interface	________
B. Number of samples collected	________
4. Field Analysis.	
A. Total hydrocarbon analysis performed	________
B. Calibration curve prepared	________
Number of components	________
Number of concentrations per component (3 required)	________

Figure 18–14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A–6 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–7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates

Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines

Method 21—Determination of volatile organic compound leaks

Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares

Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans From Stationary Sources

Method 24—Determination of volatile matter content, water content, density, volume solids, and weight solids of surface coatings

Method 24A—Determination of volatile matter content and density of printing inks and related coatings

Method 25—Determination of total gaseous nonmethane organic emissions as carbon

Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer

Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer

Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases

Method 25D—Determination of the Volatile Organic Concentration of Waste Samples

Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ‘‘Test Methods and Procedures’’ is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ‘‘subject to the approval of the Administrator’’ or as ‘‘or equivalent.’’ Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator’s disapproval of the alternative.

Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates

1.0 Scope and Application

1.1 Analytes. This method provides data reduction procedures relating to the following pollutants, but does not include any sample collection or analysis procedures.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X), including:		
Nitric oxide (NO)	10102–43–9	N/A
Nitrogen dioxide (NO_2)	10102–44–0.	
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO_2)	7499–09–05	N/A

1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO_2, and NO_X emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO_2 control devices; and (c) overall reduction of potential SO_2 emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O_2) or carbon dioxide (CO_2) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO_2 Removal Efficiency. An overall SO_2 emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO_2 control devices.

2.2.1 The sulfur removal efficiency of a fuel pretreatment system is determined by fuel sampling and analysis of the sulfur and heat contents of the fuel before and after the pretreatment system.

2.2.2 The SO_2 removal efficiency of a control device is determined by measuring the SO_2 rates before and after the control device.

2.2.2.1 The inlet rates to SO_2 control systems (or, when SO_2 control systems are not used, SO_2 emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

B_{wa} = Moisture fraction of ambient air, percent.

B_{ws} = Moisture fraction of effluent gas, percent.

%C = Concentration of carbon from an ultimate analysis of fuel, weight percent.

C_d = Pollutant concentration, dry basis, ng/scm (lb/scf)

$\%CO_{2d}, \%CO_{2w}$ = Concentration of carbon dioxide on a dry and wet basis, respectively, percent.

C_w = Pollutant concentration, wet basis, ng/scm (lb/scf).

D = Number of sampling periods during the performance test period.

E = Pollutant emission rate, ng/J (lb/million Btu).

E_a = Average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E_{ao}, E_{ai} = Average pollutant rate of the control device, outlet and inlet, respectively, for the performance test period, ng/J (lb/million Btu).

E_{bi} = Pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E_{bo} = Pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E_{ci} = Pollutant rate in combined effluent, ng/J (lb/million Btu).

E_{co} = Pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E_d = Average pollutant rate for each sampling period (*e.g.*, 24-hr Method 6B sample or 24-hr fuel sample) or for each fuel lot (*e.g.*, amount of fuel bunkered), ng/J (lb/million Btu).

E_{di} = Average inlet SO_2 rate for each sampling period d, ng/J (lb/million Btu)

E_g = Pollutant rate from gas turbine, ng/J (lb/million Btu).

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O_2.

E_{jo}, E_{ji} = Matched pair hourly arithmetic average pollutant rate, outlet and inlet, respectively, ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

E_h = Hourly average pollutant, ng/J (lb/million Btu).

E_{hj} = Hourly arithmetic average pollutant rate for hour "j," ng/J (lb/million Btu) or ppm corrected to 7 percent O_2.

EXP = Natural logarithmic base (2.718) raised to the value enclosed by brackets.

F_d, F_w, F_c = Volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

GCV = Gross calorific value of the fuel consistent with the ultimate analysis, kJ/kg (Btu/lb).

GCV_p, GCV_r = Gross calorific value for the product and raw fuel lots, respectively, dry basis, kJ/kg (Btu/lb).

%H = Concentration of hydrogen from an ultimate analysis of fuel, weight percent.

H = Total number of operating hours for which pollutant rates are determined in the performance test period.

H_b = Heat input rate to the steam generating unit from fuels fired in the steam generating unit, J/hr (million Btu/hr).

H_g = Heat input rate to gas turbine from all fuels fired in the gas turbine, J/hr (million Btu/hr).

%H_2O = Concentration of water from an ultimate analysis of fuel, weight percent.

H_r = Total numbers of hours in the performance test period (*e.g.*, 720 hours for 30-day performance test period).

K = Conversion factor, 10^{-5} (kJ/J)/(%) [10^6 Btu/million Btu].

K_c = (9.57 scm/kg)/% [(1.53 scf/lb)/%].

K_{cc} = (2.0 scm/kg)/% [(0.321 scf/lb)/%].

K_{hd} = (22.7 scm/kg)/% [(3.64 scf/lb)/%].

K_{hw} = (34.74 scm/kg)/% [(5.57 scf/lb)/%].

K_n = (0.86 scm/kg)/% [(0.14 scf/lb)/%].

K_o = (2.85 scm/kg)/% [(0.46 scf/lb)/%].

K_s = (3.54 scm/kg)/% [(0.57 scf/lb)/%].

K_w = (1.30 scm/kg)/% [(0.21 scf/lb)/%].

ln = Natural log of indicated value.

L_p,L_r = Weight of the product and raw fuel lots, respectively, metric ton (ton).

%N = Concentration of nitrogen from an ultimate analysis of fuel, weight percent.

N = Number of fuel lots during the averaging period.

n = Number of fuels being burned in combination.

n_d = Number of operating hours of the affected facility within the performance test period for each E_d determined.

n_t = Total number of hourly averages for which paired inlet and outlet pollutant rates are available within the 24-hr midnight to midnight daily period.

%O = Concentration of oxygen from an ultimate analysis of fuel, weight percent.

%O_{2d}, %O_{2w} = Concentration of oxygen on a dry and wet basis, respectively, percent.

P_s = Potential SO_2 emissions, percent.

%R_f = SO_2 removal efficiency from fuel pretreatment, percent.

%R_g = SO_2 removal efficiency of the control device, percent.

%R_{ga} = Daily geometric average percent reduction.

%R_o = Overall SO_2 reduction, percent.

%S = Sulfur content of as-fired fuel lot, dry basis, weight percent.

S_e = Standard deviation of the hourly average pollutant rates for each performance test period, ng/J (lb/million Btu).

%S_f = Concentration of sulfur from an ultimate analysis of fuel, weight percent.

S_i = Standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).

S_o = Standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).

%S_p, %S_r = Sulfur content of the product and raw fuel lots respectively, dry basis, weight percent.

$t_{0.95}$ = Values shown in Table 19–3 for the indicated number of data points n.

X_k = Fraction of total heat input from each type of fuel k.

12.2 Emission Rates of PM, SO_2, and NO_X. Select from the following sections the applicable procedure to compute the PM, S_{O2}, or NO_X emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19–1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

NOTE: Since F_w factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F_w factors are not applicable for computing E from steam generating units with wet scrubbers or with other processes that add water (*e.g.*, steam injection).

12.2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O (%O_{2d}) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_d \frac{20.9}{\left(20.9 - \%O_{2d}\right)} \qquad \text{Eq. 19-1}$$

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O_2 (%O_{2w}) and pollutant (C_w) concentrations, use either of the following:

12.2.2.1 If the moisture fraction of ambient air (B_{wa}) is measured:

$$E = C_w F_w \frac{20.9}{\left[20.9\left(1 - B_{wa}\right) - \%O_{2w}\right]} \qquad \text{Eq. 19-2}$$

Instead of actual measurement, B_{wa} may be estimated according to the procedure below.

NOTE: The estimates are selected to ensure that negative errors will not be larger than −1.5 percent. However, positive errors, or over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

12.2.2.1.1 B_{wa} = 0.027. This value may be used at any location at all times.

12.2.2.1.2 B_{wa} = Highest monthly average of B_{wa} that occurred within the previous calendar year at the nearest Weather Service Station. This value shall be determined annually and may be used as an estimate for the entire current calendar year.

12.2.2.1.3 B_{wa} = Highest daily average of Bwa that occurred within a calendar month at the nearest Weather Service Station, calculated from the data from the past 3 years. This value shall be computed for each month and may be used as an estimate for the current respective calendar month.

12.2.2.2 If the moisture fraction (B_{ws}) of the effluent gas is measured:

$$E = C_w F_d \frac{20.9}{\left[20.9\left(1 - B_{ws}\right) - \%O_{2w}\right]} \qquad \text{Eq. 19-3}$$

12.2.3 Oxygen-Based F Factor, Dry/Wet Basis.

12.2.3.1 When the pollutant concentration is measured on a wet basis (C_w) and O_2 concentration is measured on a dry basis ($\%O_{2d}$), use the following equation:

$$E = \frac{\left(C_w F_d\right)\left(20.9\right)}{\left(1 - B_{ws}\right)\left(20.9 - \%O_{2d}\right)} \qquad \text{Eq. 19-4}$$

12.2.3.2 When the pollutant concentration is measured on a dry basis (C_d) and the O_2 concentration is measured on a wet basis ($\%O_{2w}$), use the following equation:

$$E = \frac{C_d F_d 20.9}{\dfrac{\left(20.9 - \%O_{2w}\right)}{\left(1 - B_{ws}\right)}} \qquad \text{Eq. 19-5}$$

12.2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO_2 ($\%CO_{2d}$) and pollutant (C_d) concentrations, use the following equation:

$$E = C_d F_c \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-6}$$

12.2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO_2 ($\%CO_{2w}$) and pollutant (C_w) concentrations, use the following equation:

$$E = C_w F_c \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-7}$$

12.2.6 Carbon Dioxide-Based F Factor, Dry/Wet Basis.

12.2.6.1 When the pollutant concentration is measured on a wet basis (C_w) and CO_2 concentration is measured on a dry basis ($\%CO_{2d}$), use the following equation:

$$E = \frac{C_w F_c}{\left(1 - B_{ws}\right)} \frac{100}{\%CO_{2d}} \qquad \text{Eq. 19-8}$$

12.2.6.2 When the pollutant concentration is measured on a dry basis (C_d) and CO_2 concentration is measured on a wet basis ($\%CO_{2w}$), use the following equation:

$$E = C_d F_c \left(1 - B_{ws}\right) \frac{100}{\%CO_{2w}} \qquad \text{Eq. 19-9}$$

12.2.7 Direct-Fired Reheat Fuel Burning. The effect of direct-fired reheat fuel burning (for the purpose of raising the temperature of the exhaust effluent from wet scrubbers to above the moisture dew-point) on emission rates will be less than 1.0 percent and, therefore, may be ignored.

12.2.8 Combined Cycle-Gas Turbine Systems. For gas turbine-steam generator combined cycle systems, determine the emissions from the steam generating unit or the percent reduction in potential SO_2 emissions as follows:

12.2.8.1 Compute the emission rate from the steam generating unit using the following equation:

$$E_{bo} = E_{co} + \frac{H_g}{H_b}\left(E_{co} - E_g\right) \qquad \text{Eq. 19-10}$$

12.2.8.1.1 Use the test methods and procedures section of 40 CFR Part 60, Subpart GG to obtain E_{co} and E_g. Do not use F_w factors for determining E_g or E_{co}. If an SO_2 control device is used, measure E_{co} after the control device.

12.2.8.1.2 Suitable methods shall be used to determine the heat input rates to the steam generating units (H_b) and the gas turbine (H_g).

12.2.8.2 If a control device is used, compute the percent of potential SO_2 emissions (P_s) using the following equations:

$$E_{bi} = E_{ci} - \frac{H_g}{H_b}\left(E_{ci} - E_g\right) \qquad \text{Eq. 19-11}$$

$$P_s = 100\left(1 - \frac{E_{bo}}{E_{bi}}\right) \qquad \text{Eq. 19-12}$$

NOTE: Use the test methods and procedures section of Subpart GG to obtain E_{ci} and E_g. Do not use F_w factors for determining E_g or E_{ci}.

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in section 12.3.3.

12.3.1 Average F Factors. Average F factors (F_d, F_w, or F_c) from Table 19–2 in section 17.0 may be used.

12.3.2 Determined F Factors. If the fuel burned is not listed in Table 19–2 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19–2, use the procedure below:

12.3.2.1 Equations. Use the equations below, as appropriate, to compute the F factors:

$$F_d = \frac{K\left(K_{hd}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O\right)}{GCV} \qquad \text{Eq. 19-13}$$

$$F_w = \frac{K\left[K_{hw}\%H + K_c\%C + K_s\%S + K_n\%N - K_o\%O + K_w\%H_2O\right]}{GCV_w} \qquad \text{Eq. 19-14}$$

$$F_c = \frac{K\left(K_{cc}\%C\right)}{GCV} \qquad \text{Eq. 19-15}$$

NOTE: Omit the $\%H_2O$ term in the equations for F_w if %H and %O include the unavailable hydrogen and oxygen in the form of H_2O.)

12.3.2.2 Use applicable sampling procedures in section 12.5.2.1 or 12.5.2.2 to obtain samples for analyses.

12.3.2.3 Use ASTM D 3176–74 or 89 (all cited ASTM standards are incorporated by reference—see §60.17) for ultimate analysis of the fuel.

12.3.2.4 Use applicable methods in section 12.5.2.1 or 12.5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D 1826–77 or 94 (incorporated by reference—see §60.17) to determine the heat content.

12.3.3 F Factors for Combination of Fuels. If combinations of fuels are burned, use the following equations, as applicable unless otherwise specified in an applicable subpart:

$$F_d = \sum_{k=1}^{n}\left(X_k F_{dk}\right) \qquad \text{Eq. 19-16}$$

$$F_w = \sum_{k=1}^{n}\left(X_k F_{wk}\right) \qquad \text{Eq. 19-17}$$

$$F_c = \sum_{k=1}^{n}\left(X_k F_{ck}\right) \qquad \text{Eq. 19-18}$$

12.4 Determination of Average Pollutant Rates.

12.4.1 Average Pollutant Rates from Hourly Values. When hourly average pollutant rates (E_h), inlet or outlet, are obtained (*e.g.*, CEMS values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{1}{H}\sum_{j=1}^{n} E_{hj} \qquad \text{Eq. 19-19}$$

12.4.2 Average Pollutant Rates from Other than Hourly Averages. When pollutant rates are determined from measured values representing longer than 1-hour periods (*e.g.*, daily fuel sampling and analyses or Method 6B values), or when pollutant rates are determined from combinations of 1-hour and longer than 1-hour periods (*e.g.*, CEMS and Method 6B values), compute the average pollutant rate (E_a) for the performance test period (*e.g.*, 30 days) specified in the applicable regulation using the following equation:

$$E_a = \frac{\sum_{j=1}^{D}\left(n_d E_d\right)_j}{\sum_{j=1}^{D} n_{dj}} \qquad \text{Eq. 19-20}$$

12.4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E_{ga}) is computed using the following equation:

$$E_{ga} = \exp\left[\frac{1}{n_t}\sum_{j=1}^{n_t}\left[\ln\left(E_{hj}\right)\right]\right] \quad \text{Eq. 19-21}$$

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

12.5.1 Overall Percent Reduction. Compute the overall percent SO_2 reduction ($\%R_o$) using the following equation:

$$\%R_o = 100\left[1.0 - \left(1.0 - \frac{\%R_f}{100}\right)\left(1.0 - \frac{\%R_g}{100}\right)\right] \quad \text{Eq. 19-22}$$

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the averaging period (*e.g.*, 90 days) as specified in the applicable regulation using the following equation:

$$\%R_f = 100\left[1.0 - \frac{\sum_{j=1}^{N}\left(\frac{\%S_{pj}}{GCV_{pj}}\right)L_{pj}}{\sum_{j=1}^{N}\left(\frac{\%S_{rj}}{GCV_{rj}}\right)L_{rj}}\right] \quad \text{Eq. 19-23}$$

NOTE: In calculating $\%R_f$, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

12.5.2.1 Solid Fossil (Including Waste) Fuel/Sampling and Analysis.

NOTE: For the purposes of this method, raw fuel (coal or oil) is the fuel delivered to the desulfurization (pretreatment) facility. For oil, the input oil to the oil desulfurization process (*e.g.*, hydrotreatment) is considered to be the raw fuel.

12.5.2.1.1 Sample Increment Collection. Use ASTM D 2234–76, 96, 97a, or 98 (incorporated by reference—see §60.17), Type I, Conditions A, B, or C, and systematic spacing. As used in this method, systematic spacing is intended to include evenly spaced increments in time or increments based on equal weights of coal passing the collection area. As a minimum, determine the number and weight of increments required per gross sample representing each coal lot according to Table 2 or Paragraph 7.1.5.2 of ASTM D 2234. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day, then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.1.3 Gross Sample Analysis. Use ASTM D 2013–72 or 86 to prepare the sample, ASTM D 3177–75 or 89 or ASTM D 4239–85, 94, or 97 to determine sulfur content (%S), ASTM D 3173–73 or 87 to determine moisture content, and ASTM D 2015–77 (Reapproved 1978) or 96, D 3286–85 or 96, or D 5865–98 or 10 to determine gross calorific value (GCV) (all standards cited are incorporated by reference—see §60.17 for acceptable versions of the standards) on a dry basis for each gross sample.

12.5.2.2 Liquid Fossil Fuel-Sampling and Analysis. See Note under section 12.5.2.1.

12.5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D 270 or D 4177–95 (incorporated by reference—see §60.17) for each gross sample from each fuel lot.

12.5.2.2.2 Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of a product oil is the weight of product oil from one pretreatment facility and intended as one shipment (ship load, barge load, etc.). The lot size of raw oil is the weight of each crude liquid fuel type used to produce a lot of product oil.

NOTE: Alternative definitions of lot sizes may be used, subject to prior approval of the Administrator.

12.5.2.2.3 Sample Analysis. Use ASTM D 129–64, 78, or 95, ASTM D 1552–83 or 95, or ASTM D 4057–81 or 95 to determine the sulfur content (%S) and ASTM D 240–76 or 92 (all standards cited are incorporated by reference—see § 60.17) to determine the GCV of each gross sample. These values may be assumed to be on a dry basis. The owner or operator of an affected facility may elect to determine the GCV by sampling the oil combusted on the first steam generating unit operating day of each calendar month and then using the lowest GCV value of the three GCV values per quarter for the GCV of all oil combusted in that calendar quarter.

12.5.2.3 Use appropriate procedures, subject to the approval of the Administrator, to determine the fraction of total mass input derived from each type of fuel.

12.5.3 Control Device Removal Efficiency. Compute the percent removal efficiency ($\%R_g$) of the control device using the following equation:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}}{E_{ai}}\right) \qquad \text{Eq. 19-24}$$

12.5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO_2 rates and, if appropriate, the inlet SO_2 rates. The rates may be determined as hourly (E_h) or other sampling period averages (E_d). Then, compute the average pollutant rates for the performance test period (E_{ao} and E_{ai}) using the procedures in section 12.4.

12.5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO_2 rates as follows:

12.5.3.2.1 Compute the average inlet SO_2 rate (E_{di}) for each sampling period using the following equation:

$$E_{di} = K\frac{\%S}{GCV} \qquad \text{Eq. 19-25}$$

Where:

$$K = 2\times10^7\left(\frac{\text{ng SO}_2}{\%\text{S}}\right)\left(\frac{(\text{kJ})}{\text{J}}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^4\left(\frac{\text{lb SO}_2}{\%\text{S}}\right)\left(\frac{\text{Btu}}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4 to determine the average inlet SO_2 rate for the performance test period (E_{ai}).

12.5.3.2.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the "day" tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous "as bunkered" coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil "day" tank, the oil analysis from the previous day shall be used until the "day" tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

12.5.3.2.3 Use ASTM procedures specified in section 12.5.2.1 or 12.5.2.2 to determine %S and GCV.

12.5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction ($\%R_{ga}$) is computed using the following equation:

$$\%R_{ga} = 100\left[1 - \text{EXP}\left(\frac{1}{n_t}\sum_{j=1}^{n_t}\ln\frac{E_{jo}}{E_{ji}}\right)\right] \qquad \text{Eq. 19-26}$$

NOTE: The calculation includes only paired data sets (hourly average) for the inlet and outlet pollutant measurements.

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO_2 emission rates (E_{as}) to the atmosphere from a coal-fired steam generating unit when there is no SO_2 control device, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

$$E_{di} = 0.97K \frac{\%S}{GDV} \qquad \text{Eq. 19-27}$$

Where:

$$K = 2\times10^{7}\left(\frac{\text{ng } SO_2}{\%S}\right)\left(\frac{kJ}{J}\right)\left(\frac{1}{\text{kg coal}}\right)\left[2\times10^{4}\left(\frac{\text{lb } SO_2}{\%S}\right)\left(\frac{Btu}{\text{million Btu}}\right)\left(\frac{1}{\text{lb coal}}\right)\right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO_2 emission rate to the atmosphere for the performance test period (E_{ao}).

12.7 Determination of Compliance When Minimum Data Requirement Is Not Met.

12.7.1 Adjusted Emission Rates and Control Device Removal Efficiency. When the minimum data requirement is not met, the Administrator may use the following adjusted emission rates or control device removal efficiencies to determine compliance with the applicable standards.

12.7.1.1 Emission Rate. Compliance with the emission rate standard may be determined by using the lower confidence limit of the emission rate (E_{ao}*) as follows:

$$E_{ao}^{*} = E_{ao} - t_{0.95} S_o \qquad \text{Eq. 19-28}$$

12.7.1.2 Control Device Removal Efficiency. Compliance with the overall emission reduction ($\%R_o$) may be determined by using the lower confidence limit of the emission rate (E_{ao}*) and the upper confidence limit of the inlet pollutant rate (E_{ai}*) in calculating the control device removal efficiency ($\%R_g$) as follows:

$$\%R_g = 100\left(1.0 - \frac{E_{ao}^{*}}{E_{ai}^{*}}\right) \qquad \text{Eq. 19-29}$$

$$E_{ai}^{*} = E_{ai} + t_{0.95} S_i \qquad \text{Eq. 19-30}$$

12.7.2 Standard Deviation of Hourly Average Pollutant Rates. Compute the standard deviation (S_e) of the hourly average pollutant rates using the following equation:

$$S_e = \sqrt{\frac{1}{H} - \frac{1}{H_r}}\sqrt{\frac{\sum_{j=1}^{H}\left(E_{hj} - E_a\right)^2}{H-1}} \qquad \text{Eq. 19-31}$$

Equation 19–19 through 19–31 may be used to compute the standard deviation for both the outlet (S_o) and, if applicable, inlet (S_i) pollutant rates.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	10^9
mg/scm	ng/scm	10^6
lb/scf	ng/scm	1.602×10^{13}

TABLE 19–1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO_2	ng/scm	2.66×10^6
ppm NO_X	ng/scm	1.912×10^6
ppm SO_2	lb/scf	1.660×10^{-7}
ppm NO_X	lb/scf	1.194×10^{-7}

TABLE 19–2—F FACTORS FOR VARIOUS FUELS[1]

Fuel Type	F_d		F_w		F_c	
	dscm/J	dscf/10^6 Btu	wscm/J	wscf/10^6 Btu	scm/J	scf/10^6 Btu
Coal:						
Anthracite[2]	2.71×10^{-7}	10,100	2.83×10^{-7}	10,540	0.530×10^{-7}	1,970
Bituminus[2]	2.63×10^{-7}	9,780	2.86×10^{-7}	10,640	0.484×10^{-7}	1,800
Lignite	2.65×10^{-7}	9,860	3.21×10^{-7}	11,950	0.513×10^{-7}	1,910
Oil[3]	2.47×10^{-7}	9,190	2.77×10^{-7}	10,320	0.383×10^{-7}	1,420
Gas:.						
Natural	2.34×10^{-7}	8,710	2.85×10^{-7}	10,610	0.287×10^{-7}	1,040
Propane	2.34×10^{-7}	8,710	2.74×10^{-7}	10,200	0.321×10^{-7}	1,190
Butane	2.34×10^{-7}	8,710	2.79×10^{-7}	10,390	0.337×10^{-7}	1,250
Wood	2.48×10^{-7}	9,240			0.492×10^{-7}	1,830
Wood Bark	2.58×10^{-7}	9,600			0.516×10^{-7}	1,920
Municipal	2.57×10^{-7}	9,570			0.488×10^{-7}	1,820
Solid Waste						

[1] Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg)
[2] As classified according to ASTM D 388.
[3] Crude, residual, or distillate.

TABLE 19–3—VALUES FOR $T_{0.95}$*

n[1]	$t_{0.95}$	n[1]	$t_{0.95}$	n[1]	$t_{0.95}$
2	6.31	8	1.89	22–26	1.71
3	2.42	9	1.86	27–31	1.70
4	2.35	10	1.83	32–51	1.68
5	2.13	11	1.81	52–91	1.67
6	2.02	12–16	1.77	92–151	1.66
7	1.94	17–21	1.73	152 or more	1.65

[1] The values of this table are corrected for n-1 degrees of freedom. Use n equal to the number (H) of hourly average data points.

METHOD 20—DETERMINATION OF NITROGEN OXIDES, SULFUR DIOXIDE, AND DILUENT EMISSIONS FROM STATIONARY GAS TURBINES

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen oxides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO_X) as nitrogen dioxide:	10102–43–9	Typically <2% of Calibration Span.
Nitric oxide (NO)	10102–44–0	
Nitrogen dioxide NO_2.		
Diluent oxygen (O_2) or carbon dioxide (CO_2)		Typically <2% of Calibration Span.
Sulfur dioxide (SO_X)	7446–09–5	Typically <2% of Calibration Span.

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State Implementation Plans and permits where measuring SO_2, NO_X, CO_2, and/or O_2 concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

1.3 Data Quality Objectives. How good must my collected data be? Refer to section 1.3 of Method 7E.

2.0 Summary of Method

In this method, NO_X, O_2 (or CO_2), and SO_X are measured using the following methods found in appendix A to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).

(e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

Refer to section 3.0 of Method 7E for the applicable definitions.

4.0 Interferences

Refer to section 4.0 of Methods 3A, 6C, and 7E as applicable.

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

The measurement system design is shown in Figure 7E–1 of Method 7E. Refer to the appropriate methods listed in section 2.0 for equipment and supplies.

7.0 Reagents and Standards

Refer to the appropriate methods listed in section 2.0 for reagents and standards.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Site and Sampling Points. Follow the procedures of section 8.1 of Method 7E. For the stratification test in section 8.1.2, determine the diluent-corrected pollutant concentration at each traverse point.

8.2 Initial Measurement System Performance Tests. You must refer to the appropriate methods listed in section 2.0 for the measurement system performance tests as applicable.

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C, or section 8.2.7 of Method 7E (as appropriate).

8.4 Sample Collection. You must follow the procedures of section 8.4 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

8.5 Post-Run System Bias Check, Drift Assessment, and Alternative Dynamic Spike Procedure. You must follow the procedures of sections 8.5 and 8.6 of the appropriate methods listed in section 2.0. A test run must have a duration of at least 21 minutes.

9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis in section 12.0 of the appropriate method listed in section 2.0. Follow the procedures in section 12.0 of Method 19 for calculating fuel-specific F factors, diluent-corrected pollutant concentrations, and emission rates.

13.0 Method Performance

The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Refer to section 16.0 of the appropriate method listed in section 2.0 for alternative procedures.

17.0 References

Refer to section 17.0 of the appropriate method listed in section 2.0 for references.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Refer to section 18.0 of the appropriate method listed in section 2.0 for tables, diagrams, flowcharts, and validation data.

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile Organic Compounds (VOC).	No CAS number assigned.

1.2 Scope. This method is applicable for the determination of VOC leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.3 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 portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in section 6.0. A leak definition concentration based on a reference compound is specified in each applicable regulation. This method is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rate from individual sources.

3.0 Definitions

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

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

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

3.4 *No detectable emission* means a local VOC concentration at the surface of a leak source, adjusted for local VOC ambient concentration, that is less than 2.5 percent of the specified leak definition concentration. that indicates that a VOC emission (leak) is not present.

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

3.6 *Response factor* means the ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the applicable regulation.

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

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.

5.2 Hazardous Pollutants. Several of the compounds, leaks of which may be determined by this method, may be irritating or corrosive to tissues (*e.g.*, heptane) or may be toxic (*e.g.*, benzene, methyl alcohol). Nearly all are fire hazards. Compounds in emissions should be determined through familiarity with the source. Appropriate precautions can be found in reference documents, such as reference No. 4 in section 16.0.

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

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

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

6.3 The scale of the instrument meter shall be readable to ±2.5 percent of the specified leak definition concentration.

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft^3/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm (¼ in) in outside diameter, with a single end opening for admission of sample.

6.6 The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the National Electrical Code by the National Fire Prevention Association or other applicable regulatory code for operation in any explosive atmospheres that may be encountered in its use. The instrument shall, at a minimum, be intrinsically safe for Class 1, Division 1 conditions, and/or Class 2, Division 1 conditions, as appropriate, as defined by the example code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

7.0 Reagents and Standards

7.1 Two gas mixtures are required for instrument calibration and performance evaluation:

7.1.1 Zero Gas. Air, less than 10 parts per million by volume (ppmv) VOC.

7.1.2 Calibration Gas. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration approximately equal to the applicable leak definition specified in the regulation.

7.2 Cylinder Gases. If cylinder calibration gas mixtures are used, they must be analyzed and certified by the manufacturer to be within 2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life.

7.3 Prepared Gases. Calibration gases may be prepared by the user according to any accepted gaseous preparation procedure that will yield a mixture accurate to within 2 percent. Prepared standards must be replaced each day of use unless it is demonstrated that degradation does not occur during storage.

7.4 Mixtures with non-Reference Compound Gases. Calibrations may be performed using a compound other than the reference compound. In this case, a conversion factor must be determined for the alternative compound such that the resulting meter readings during source surveys can be converted to reference compound results.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Instrument Performance Evaluation. Assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

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

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1–3 of section 17.0.

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

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

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

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

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

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

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

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

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

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

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

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

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

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—“No Detectable Emission”. Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

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

11.0 Analytical Procedures [Reserved]

12.0 Data Analyses and Calculations [Reserved]

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2–81051. September 1981.

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

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

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

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

METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

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

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

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (*e.g.*, road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

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.

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

7.0 Reagents and Supplies [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transfer [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (*i.e.*, outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22–1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22–2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (*i.e.,* the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified observed period) is observed in a shorter time period. In other words, if the regulation prohibits emissions for more than 6 minutes in any hour, then observations may (optional) be stopped after an emission time of 6 minutes is exceeded. Similarly, when the regulation is expressed as an emission frequency and the regulation prohibits emissions for greater than 10 percent of the time in any hour, then observations may (optional) be terminated after 6 minutes of emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA–340/1–75–007. April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources. EPA Publication No. EPA–650/4–74–005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

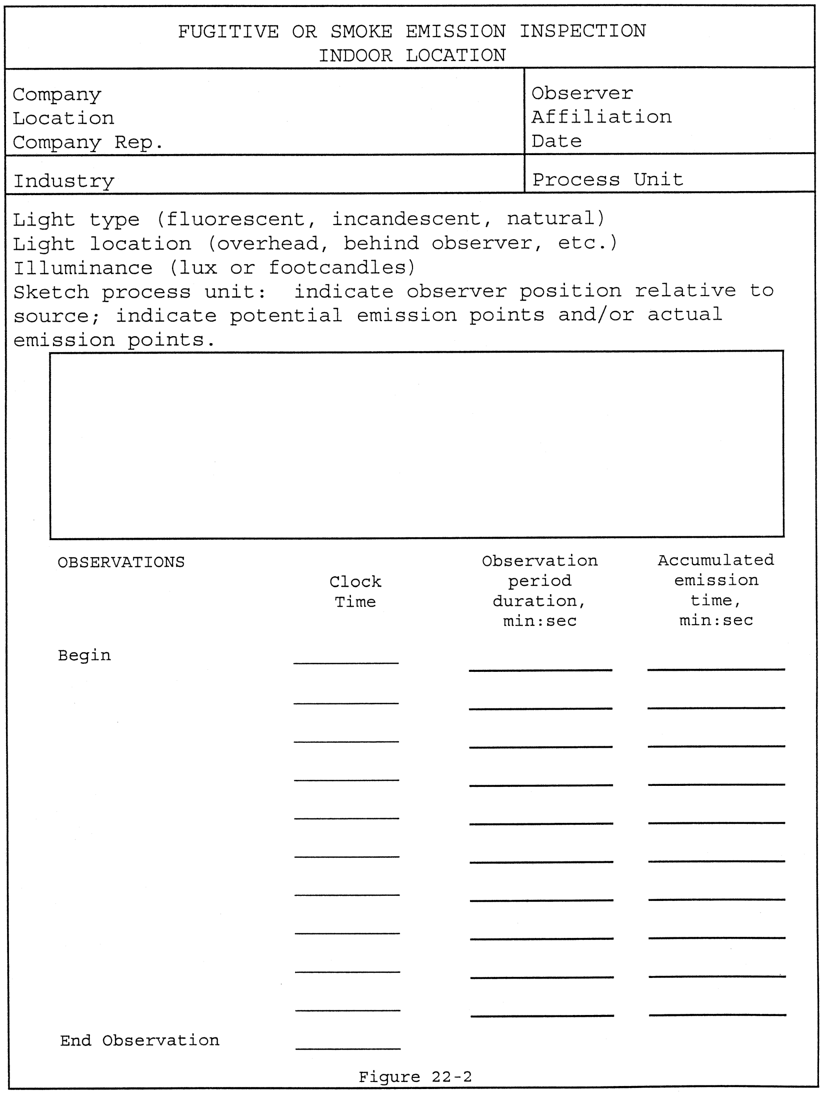
FUGITIVE OR SMOKE EMISSION INSPECTION
OUTDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Sky Conditions Precipitation	Wind Direction Wind Speed
Industry	Process Unit

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

OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation	________	________	________
	________	________	________
	________	________	________
	________	________	________
	________	________	________
	________	________	________
	________	________	________
	________	________	________
	________	________	________
	________		
End Observation		________	________
	________		

Figure 22-1



FUGITIVE OR SMOKE EMISSION INSPECTION
INDOOR LOCATION

Company Location Company Rep.	Observer Affiliation Date
Industry	Process Unit

Light type (fluorescent, incandescent, natural)
Light location (overhead, behind observer, etc.)
Illuminance (lux or footcandles)
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.

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

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and

PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23–1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

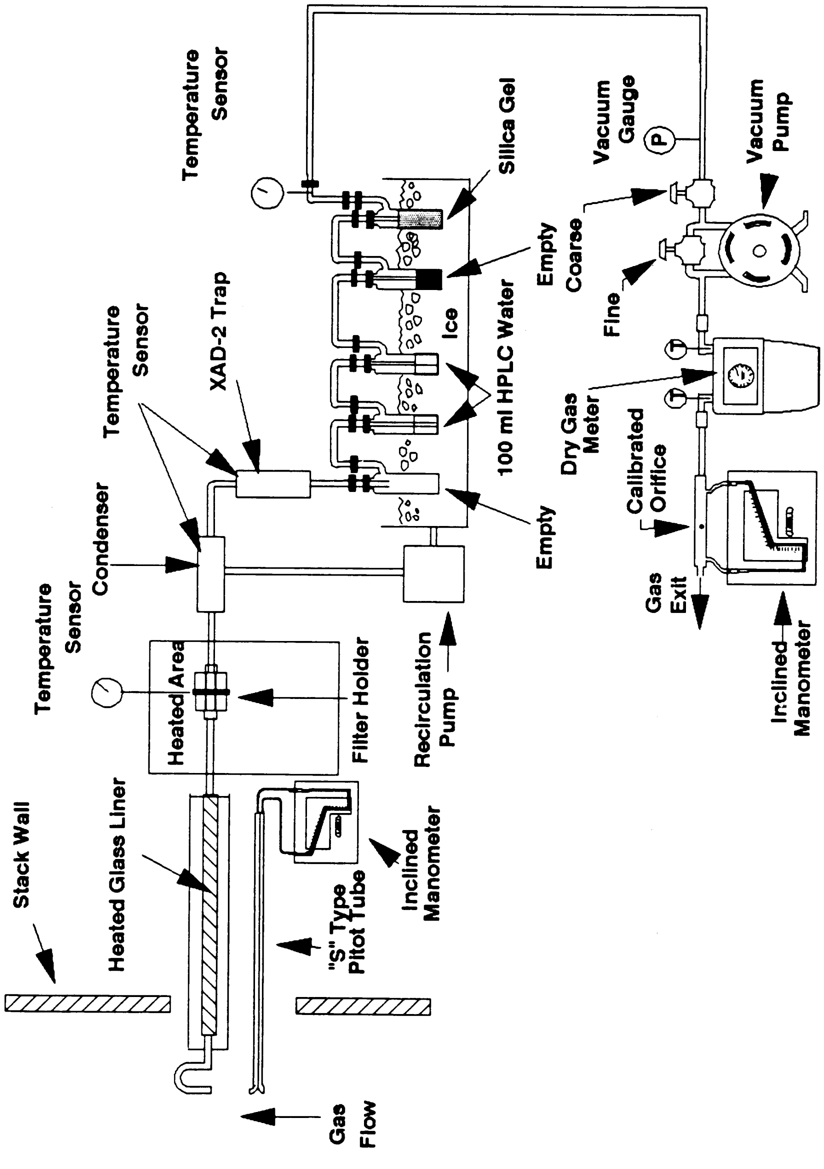


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23–2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23–2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

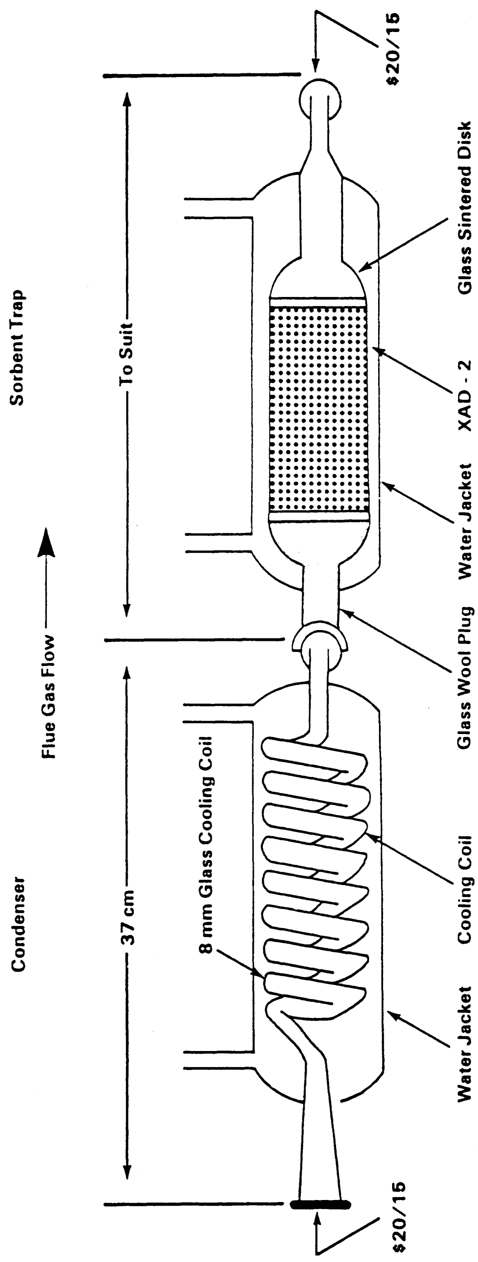


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB–5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see § 60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD–2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX–21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Internal Standards'' in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Surrogate Standards'' in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading ''Recovery Standards'' in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the ''Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.'' Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the trap. Add 100 µl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23–1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the ‘‘Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples.’’ All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD–2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD–2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD–2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD–2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1–5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX–21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX–21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 μl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 μl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 μl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB–5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB–225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1–2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.
2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.
3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.
4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.
5. The signal to noise ratio for all monitored ions must be greater than 2.5.
6. The confirmation of 2, 3, 7, 8–TCDD and 2, 3, 7, 8–TCDF shall satisfy all of the above identification criteria.
7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$–2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$–1,2,3,4–TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$–1,2,3,7,8,9–HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8–TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i{}^* A_i}{A_i{}^* RRF_i V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}{}^* m_{rs}}{A_{rs} m_{ci}{}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i{}^* m_{rs}}{A_{rs} RF_{rs} m_i{}^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}{}^* m_s}{A_{cis} m_{ci}{}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i{}^*}{A_i{}^* RRF_s m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\ A_{ai} m_i{}^*}{A_{ci}{}^* RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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3. Thompson, J. R. (ed.). Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards:					
${}^{13}C_{12}$-1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
${}^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	${}^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	${}^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	${}^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	${}^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	${}^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	${}^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M + 2	${}^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	${}^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	${}^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M + 2	${}^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	${}^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	${}^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	${}^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M + 2	${}^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M + 2	${}^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M + 4	${}^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M + 4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M + 2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M + 4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M + 2	${}^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M + 4	${}^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M + 4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
${}^{13}C$ = 13.003355
F = 18.9984
O = 15.994915
${}^{35}Cl$ = 34.968853
${}^{37}Cl$ = 36.965903

S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.
[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds	No CAS Number assigned
Water.	7732–18–5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

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.

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see §60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475–60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369–81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792–79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017–81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457–85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403–93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419–00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings). The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured parameters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to 225 cm^2 (35 in^2) then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ±1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 + 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ±0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ±5 °C (230 ±9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ±5 °C (230 ±9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_V following Equation 24–2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water-or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water-or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (w_w).

11.3.3 Coating Density. Determine the density (Dc, kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

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

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD–14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm^2, (in^2).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm^3 (g/in^3).

F = Manufacturer's recommended film thickness, cm (in).
W_o = Weight fraction of nonaqueous volatile matter, g/g.
W_s = Weight fraction of solids, g/g.
W_v = Weight fraction of the volatile matter, g/g.
W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = F\,A\,D_c \qquad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.

12.4.1 Solvent-borne Coatings.

$$W_o = W_v \qquad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \qquad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \qquad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \qquad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24–1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24–1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W_v	±0.015 $\bar{\bar{W}}_v$	±0.047 $\bar{\bar{W}}_v$
Water content, W_w	±0.029 $\bar{\bar{W}}_w$	±0.075 $\bar{\bar{W}}_w$
Density, D_c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reducible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to 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.

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) and an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 ±2 °C (248 ±4 °F) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475–60, 80, or 90 (incorporated by reference—see § 60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475–60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of 510 ±51 mm Hg (20 ±2 in. Hg) and a temperature of 120 ±2 °C (248 ±4 °F) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of 120 ±2 °C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

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

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average ($\bar{W}_o$) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \qquad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.
2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.
3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.
4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA–340/1–91–010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA–340/1–91–011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.
6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

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

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

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

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

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

2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2, and CH_4; the NMO are oxidized to CO_2, reduced to CH_4, and measured by an 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

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2. Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

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.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25–1). The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (¼-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25–1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (15⁄16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ±3 °C (250 ±5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25–2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11½ in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 9½ in.). The inner box is supported by 13-mm (½-in.) phenolic rods. The void space between the boxes is filled with ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (⅜-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

25–3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm^3 before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm^3/min (0.13 to 0.21 ft^3/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft^3).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

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

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25–4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3⁄8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3⁄8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1⁄4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO_2 concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft^3) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-μl and 50-μl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25–7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25–5 and 25–6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO_2, and CH_4 from NMO, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the NMO to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3⁄8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1⁄8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1⁄4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1⁄8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1⁄8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

6.3.1.5.1 Linearity. A linear response (±5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH_4. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

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

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

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

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

7.0 Reagents and Standards

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Dry Ice. Solid CO2, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986–71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O_2) containing less than 1 ppm CO_2 and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H_2), at least 99.999 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

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

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

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO_2 Calibration Gases. Three gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 1 percent CO_2, and 20 ppm C_3H_8, prepared in air.

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

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

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

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO_2 concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling system as shown in Figure 25–1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25–1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm^3/min (0.13 and 0.21 ft^3/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25–8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O_2 Blank Check. Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to check for contamination. Treat the gas cylinders as noncondensible gas samples, and analyze according to the procedure in section 11.2.3. Add together any measured CH_4, CO, CO_2, 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 ⅛″ 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 CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 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 O_2 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 CO_2 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 ±5 percent and the relative standard deviation is less than 2 percent for each set of triplicate injections.

10.1.1.3.1 50 μl hexane.

10.1.1.3.2 10 μl hexane.

10.1.1.3.3 50 μl decane.

10.1.1.3.4 10 μl 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 and 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 CO_2 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 CO_2 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 analysis of each set of samples, or on a daily basis, whichever is more stringent:

10.2.1 CO_2 Response Factor. Inject triplicate samples of the high level CO_2 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 CO_2 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 CO_2 content. The system background is acceptable if the CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 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 CO_2 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.

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 CO_2 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 CO_2 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 CO_2 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 CO_2 concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO_2 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 CO_2 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 O_2. The column oven is heated to 85 °C (185 °F). The order of elution for the sample from the column is CO, CH_4, CO_2, 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 CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 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 condensible organic material (C_{cm}) measured as CO_2 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_{tm}).

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 condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
F = Sampling flow rate, cc/min.
L = Volume of liquid injected, µl.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = TGNMO mass concentration of the effluent, mg C/dsm^3.
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_{ti} = Gas sample tank pressure before sampling, mm Hg absolute.
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.
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_{ti} = Sample tank temperature before sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing, °K.
V = Sample tank volume, m^3.
V_t = Sample train volume, cc.
V_v = Intermediate collection vessel volume, m^3.
V_s = Gas volume sampled, dsm^3.
x_i = Individual measurements.
$\bar{x}$ = Mean value.

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:

$$\Delta P = 0.01 \, \frac{F P_b \Theta}{V_t} \qquad \text{Eq. 25-1}$$

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

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

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

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

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

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

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

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

12.7 Percent Recovery. Calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system using Equation 25–6:

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

where K = 1.604 (°K)(g-mole)(%)/(mm Hg)(ml)(m^3)(ppm).

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

$$RSD = \frac{100}{\bar{x}} \left[\frac{\sum_{i=1}^{n} \left(x_i - \bar{x} \right)^2}{n-1} \right]^{\frac{1}{2}} \qquad \text{Eq. 25-7}$$

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.

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

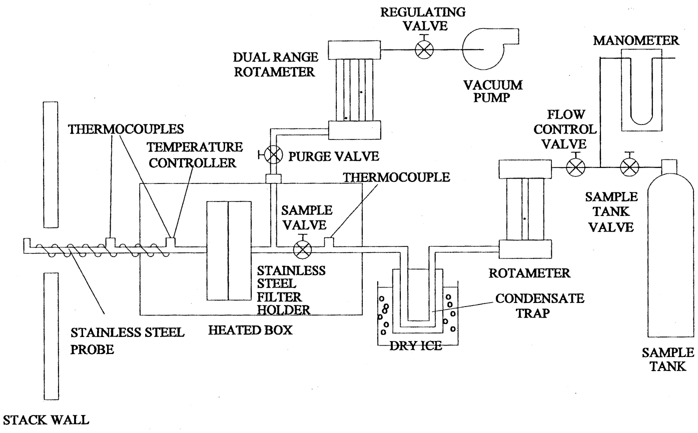


Figure 25-1. Sampling Train

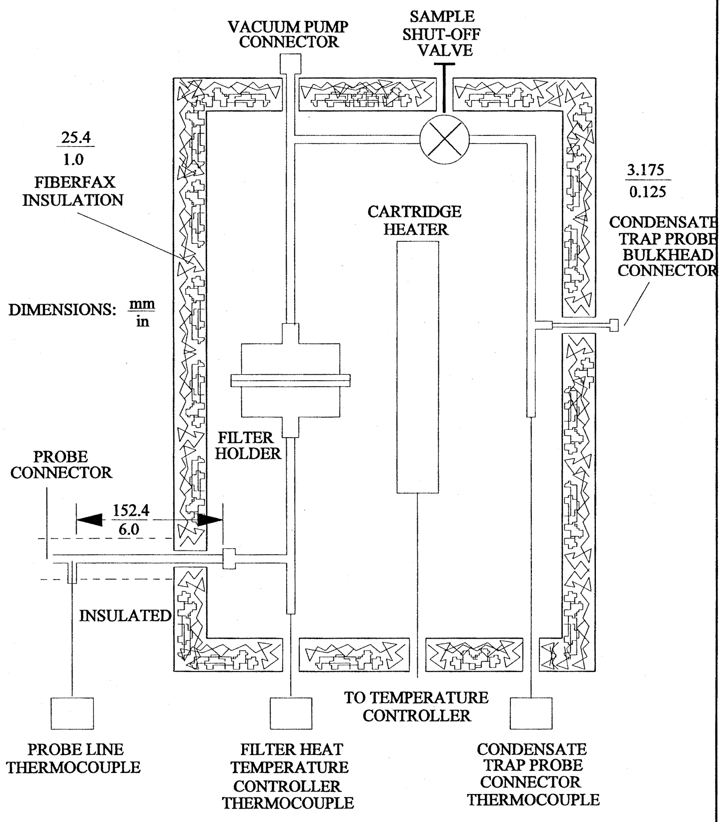


Figure 25-2. Out-of-stack Filter Box

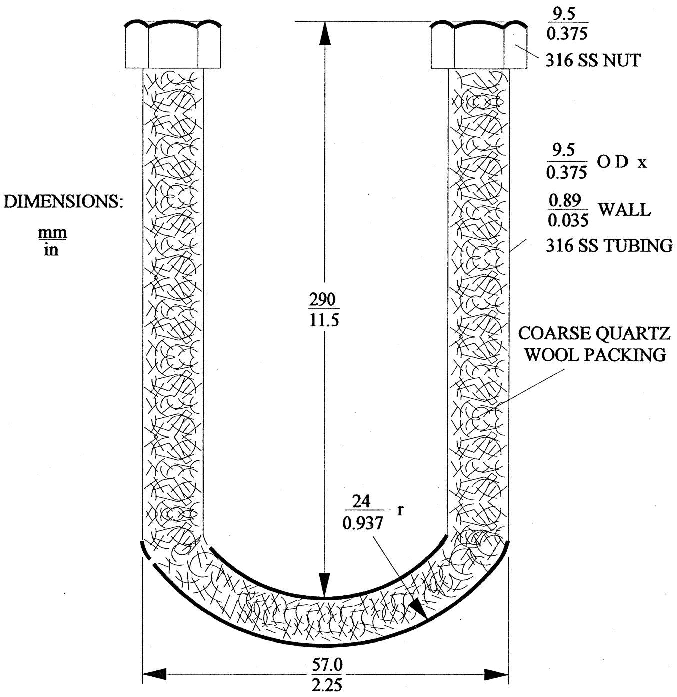


Figure 25-3. Condensate Trap

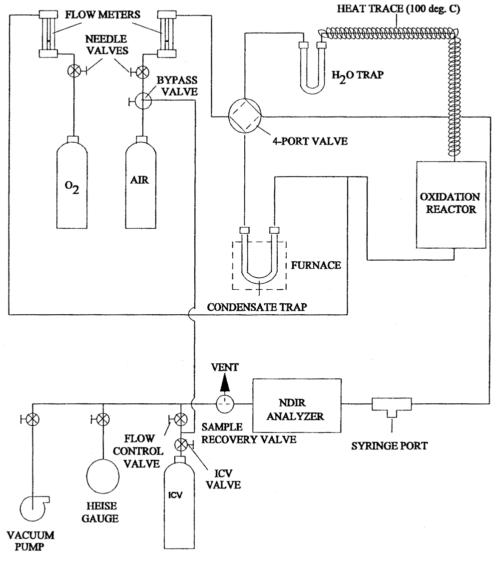


Figure 25-4. Condensate Recovery System

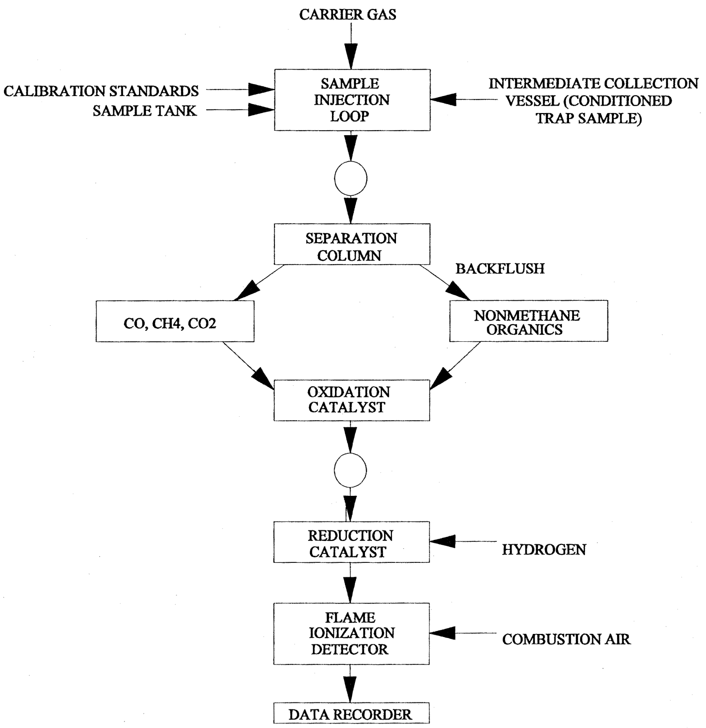


Figure 25-5. Simplified Schematic of Nonmethane Organic (NMO) Analyzer

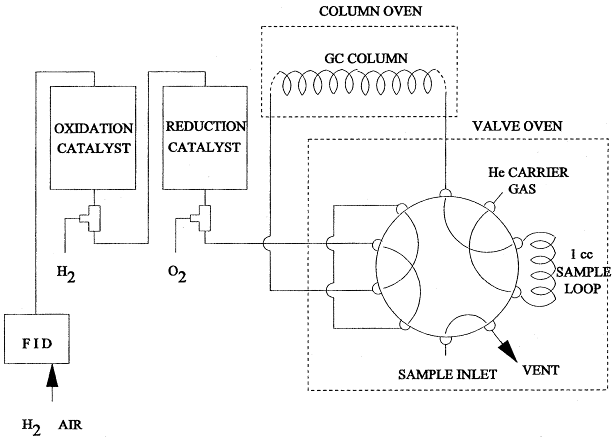


Figure 25-6. Nonmethane Organic Analyzer (NMO)

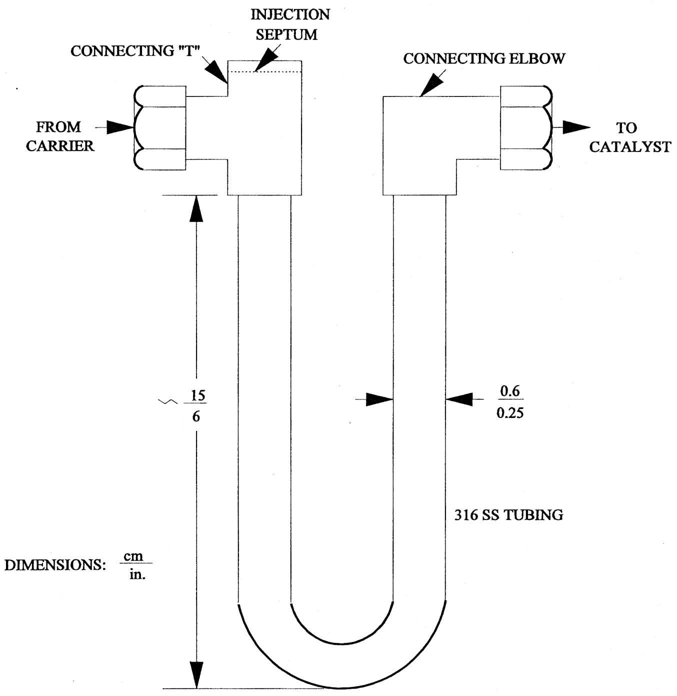
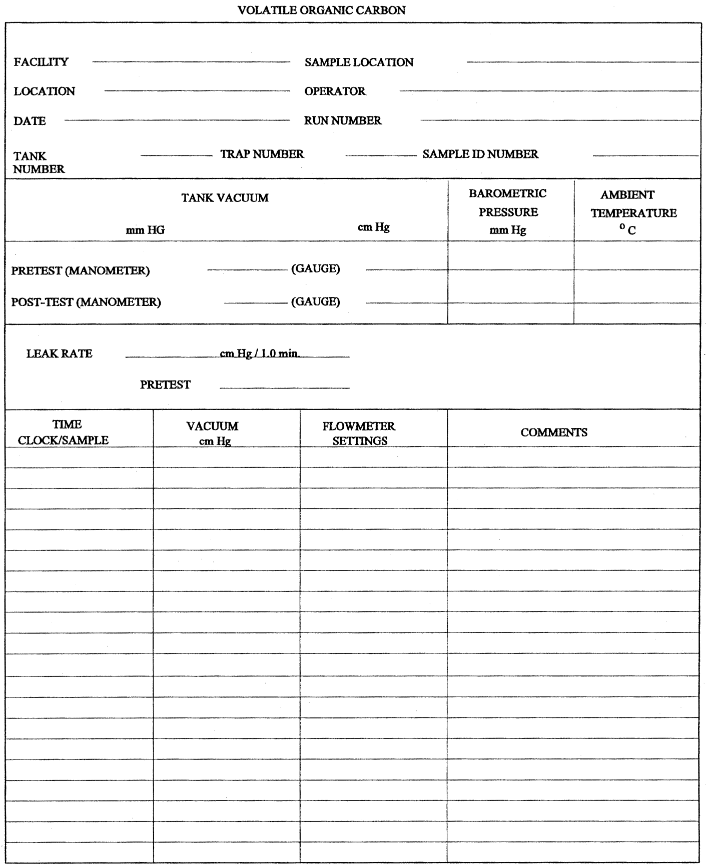


Figure 25-7. Liquid Sample Injection Unit



VOLATILE ORGANIC CARBON

FACILITY ______ SAMPLE LOCATION ______
LOCATION ______ OPERATOR ______
DATE ______ RUN NUMBER ______
TANK NUMBER ______ TRAP NUMBER ______ SAMPLE ID NUMBER ______

TANK VACUUM mm HG	 cm Hg	BAROMETRIC PRESSURE mm Hg	AMBIENT TEMPERATURE ° C
PRETEST (MANOMETER) ______	(GAUGE) ______		
POST-TEST (MANOMETER) ______	(GAUGE) ______		

LEAK RATE ______ cm Hg / 1.0 min. ______
PRETEST ______

TIME CLOCK/SAMPLE	VACUUM cm Hg	FLOWMETER SETTINGS	COMMENTS

Figure 25-8. Example Field Data Form

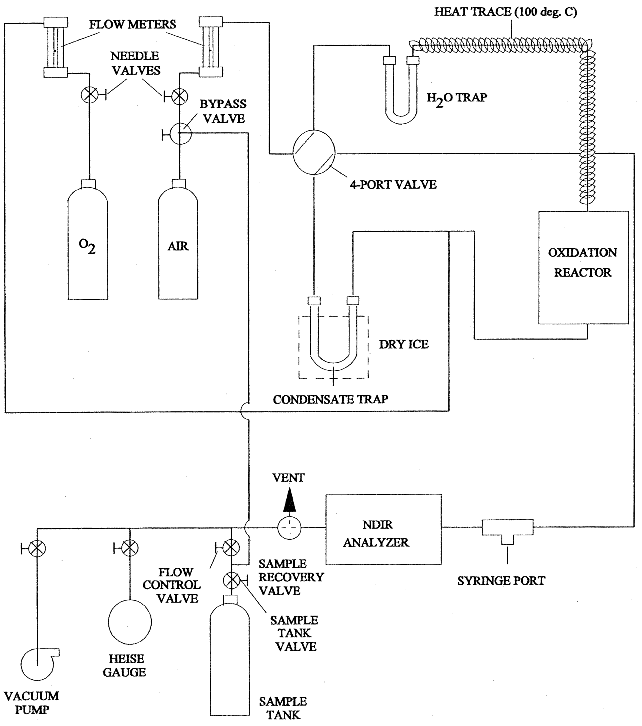


Figure 25-9. Condensate Recovery System, CO2 Purge

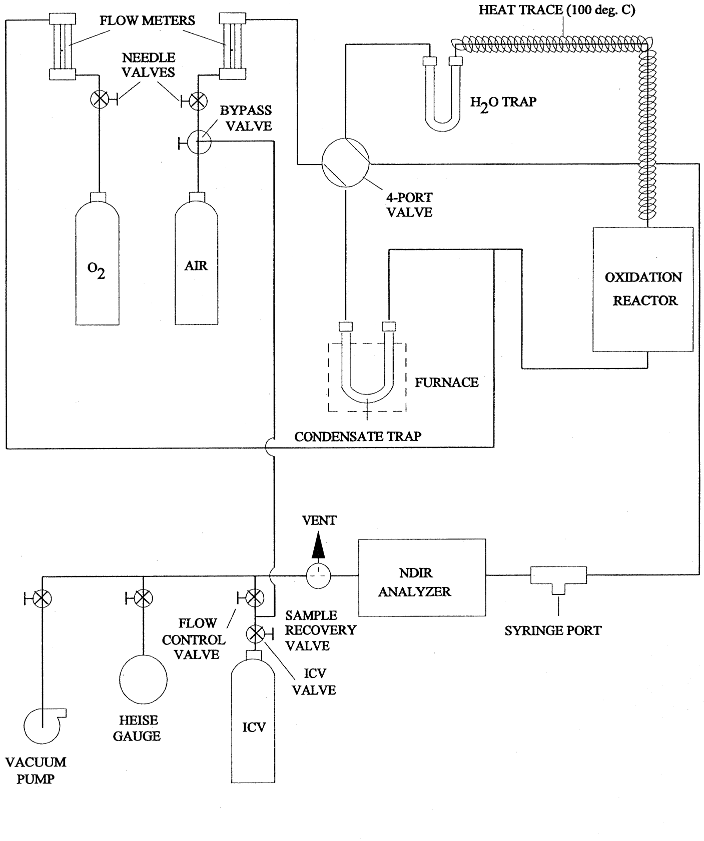


Figure 25-10. Condensate Recovery System, Collection of Trap Organics

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 know 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 ≥110 °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 °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 to the analyzer. The sample line should be heated (≥110 °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 H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

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.

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 particulate, note on the recording chart, periods of process interruption or cyclic operation.

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.

11.0 Analytical Procedure

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

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.

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

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.
= 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

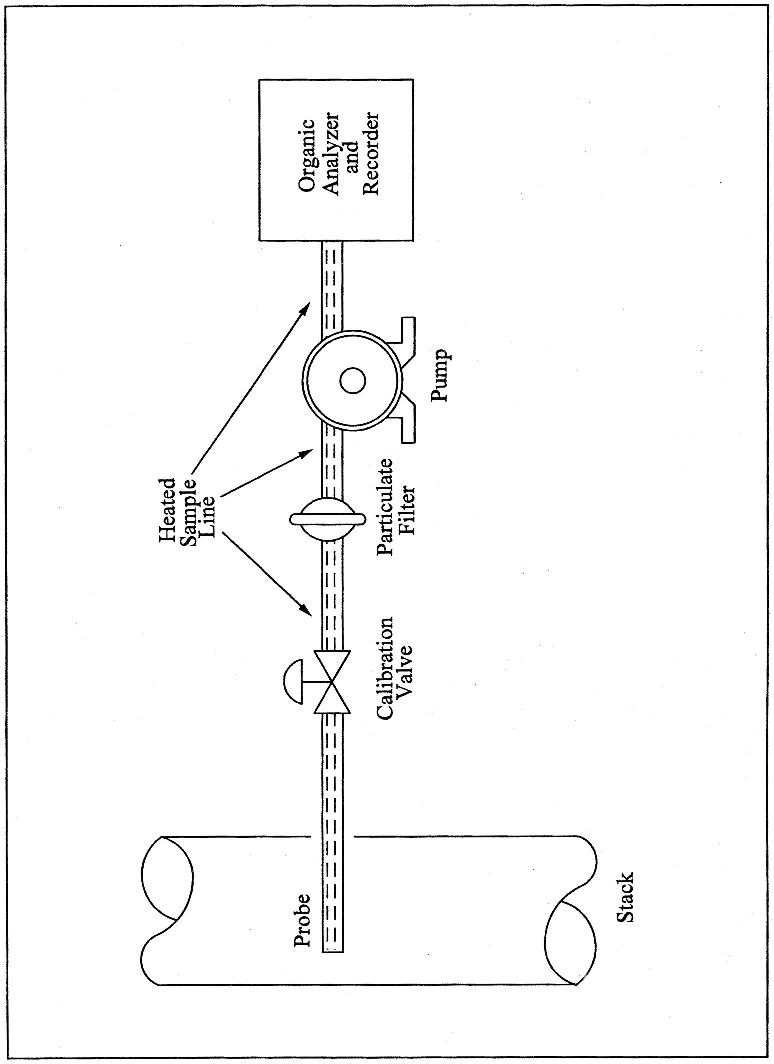


Figure 25A-1. Organic Concentration Measurement System.

METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE 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 nondispersive 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 injecting a portion of the gas into a gas chromatographic column to separate the NMOC from carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4); the NMOC are oxidized to CO_2, reduced to CH_4, 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 H_2O) in the range of 0 to 1,100 mm Hg (0 to 590 in H_2O).

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 H_2O).

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 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 H_2O) 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 hours for the landfill gases to equilibrate inside the augured probe before sampling.

8.2.3 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. H_2O) absolute pressure with helium, 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 N_2 in each cylinder. The presence of N_2 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 N_2 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_2.	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 CO_2 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 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 CO_2 in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO_2 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_{tm}.

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} = N_2 concentration in the diluted sample gas.
C_{mN2} = Measured N_2 concentration, fraction in landfill gas.
C_{mOx} = Measured Oxygen concentration, fraction in landfill gas.
C_{Ox} = Oxygen concentration in the diluted sample gas.
C_t = Calculated NMOC concentration, ppmv C equivalent.
C_{tm} = 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_{ti} = Gas sample tank pressure after evacuation, mm Hg absolute.
P_w = Vapor pressure of H_2O (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_{ti} = 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.

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

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

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

12.4 Oxygen Concentration in the landfill gas. Use equation 25C–3 to calculate the measured concentration of oxygen in the original landfill gas.

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

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.

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

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.

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

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

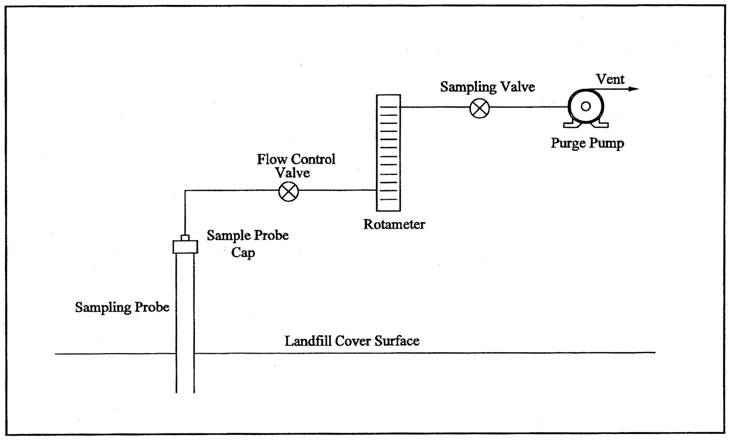


Figure 25C-1. Schematic of Sampling Probe Purging System

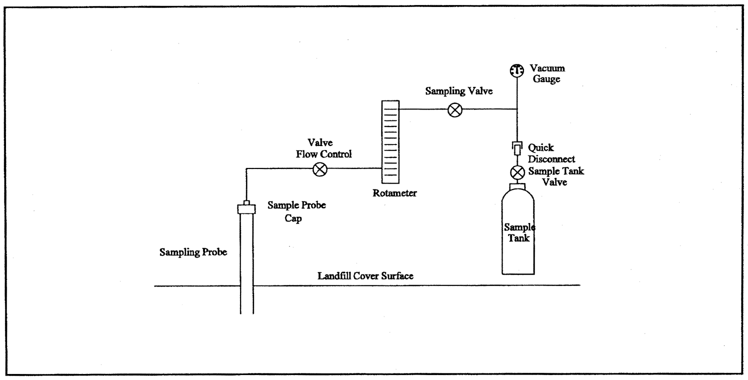


Figure 25C-2. Schematic of Sampling Train.

TABLE 25C–1—MOISTURE CORRECTION

Temperature, °C	Vapor Pressure of H_2O, mm Hg	Tempera-ture, °C	Vapor Pressure of H_2O, 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
16	13.6	30	31.8

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.

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 ±2 °C (167 ±3.6 °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 ±0.06 L/min (0.2 ±0.002 ft^3/min) The other capable of maintaining a calibration gas flow rate of 1–100 mL/min (0.00004–0.004 ft^3/min).

6.2.1.7 Rotameter. For monitoring the air flow through the purging system (0–10 L/min)(0–0.4 ft^3/min).

6.2.1.8 Sample Splitters. Two heated flow restrictors (placed inside oven or heated to 120 ±10 °C (248 ±18 °F)). At a purge rate of 6 L/min (0.2 ft^3/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 ft^3/min) and to the ELCD will be 15 mL/min (0.0005 ft^3/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.

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 ft^3/min).

NOTE: A ¼-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 ft^3/min) for 2 hours. The cleaned PEG must be stored under a 1 to 2 L/min (0.04 to 0.07 ft^3/min) nitrogen purge until use. The purge 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 (N_2), 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 (H_2). Zero grade H_2, 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 $KMnO_4$ 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.

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_{st}). 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_{sf}). 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 μL 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 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 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 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 ±2 °C (167 ±3.6 °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 ±2 °C (167 ±3.6 °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_t = Average daily response factor of the FID, mg CH_4/counts.

Dr_{th} = 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_{st} = 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_{vc} = Percent 1,1-dichloroethylene in calibration gas (L/L).

Q_c = Flow rate of calibration gas, L/min.

t_c = 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.

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

12.3 Concentration of Chloride in the Calibration Gas.

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

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

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

12.5 Mass of Chloride in a Calibration Run.

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

12.6 FID Response Factor, mg/counts.

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

12.7 ELCD Response Factor, mg/counts.

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

12.8 Mass of Carbon in the Sample.

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

12.9 Mass of Chloride in the Sample.

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

12.10 Mass of Volatile Organics in the Sample.

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

12.11 Relative Standard Deviation.

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

12.12 Mass of Sample.

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

12.13 Concentration of Volatile Organics in Waste.

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

12.14 Weighted Average VO Concentration of Multi-phase Waste.

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

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

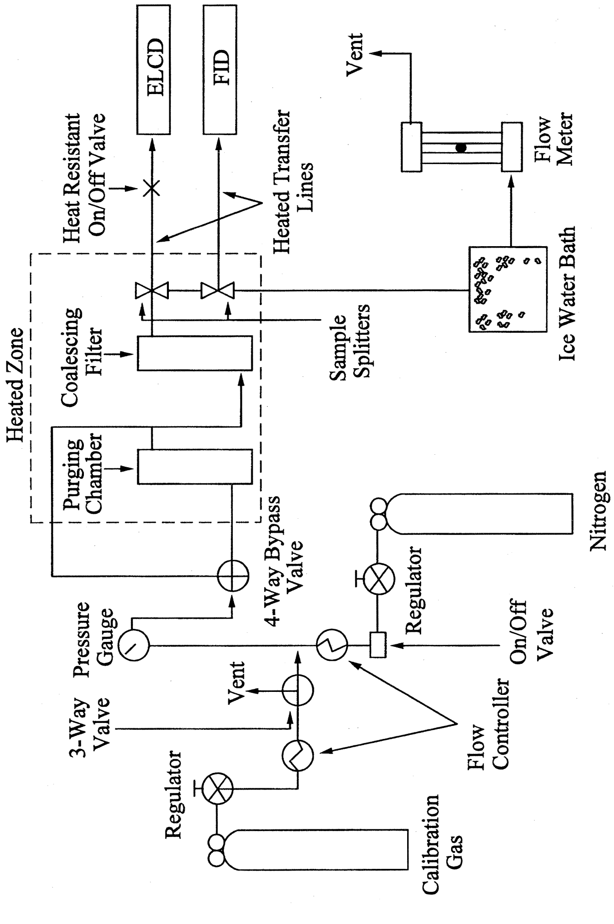


Figure 25D-1. Schematic of Purging Apparatus.

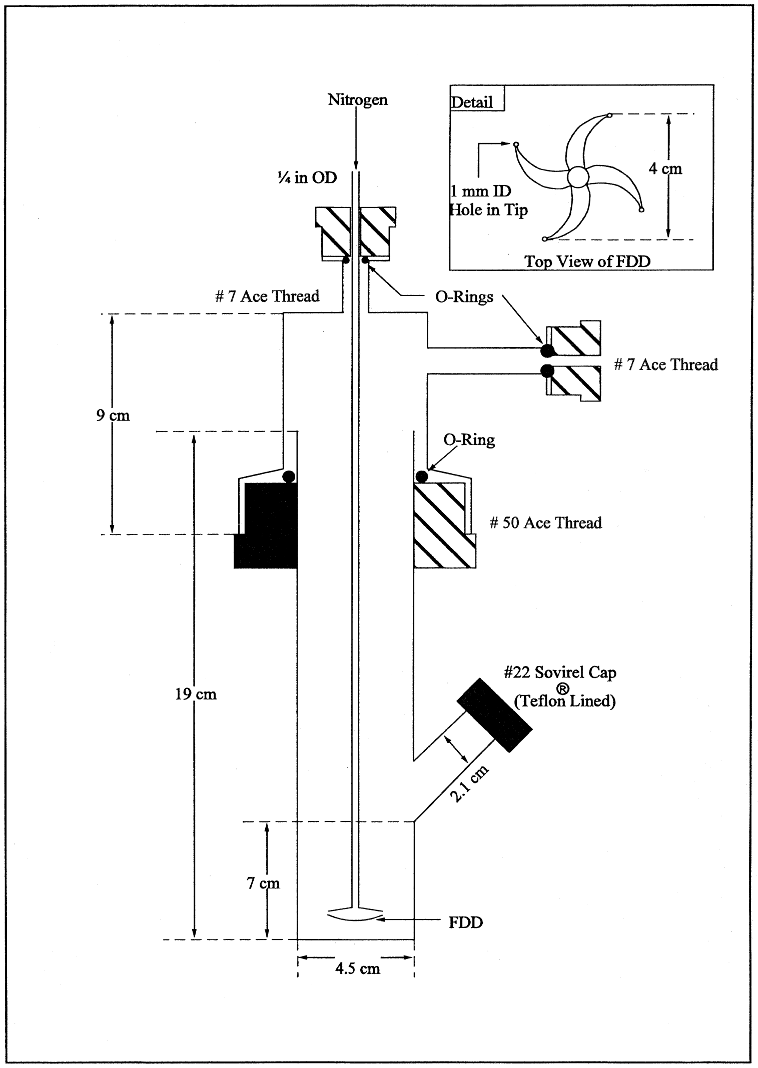
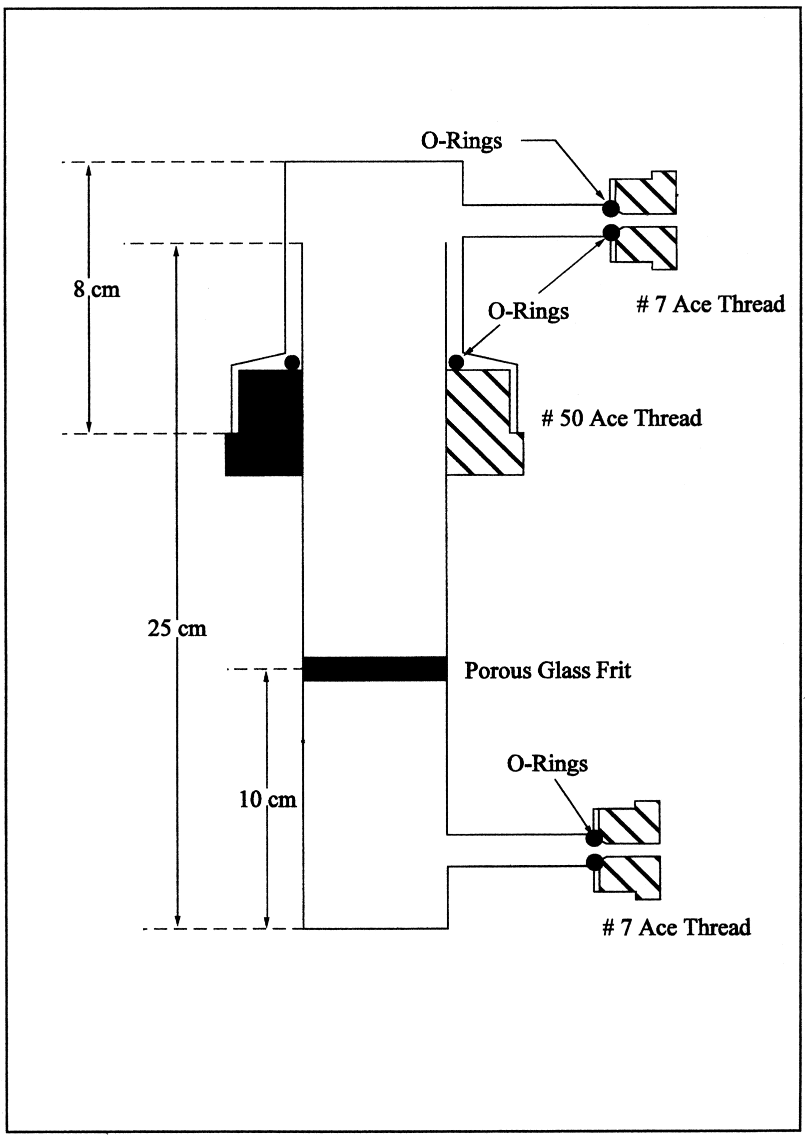


Figure 25D-2. Purging Lance.


O-Rings
8 cm
O-Rings
7 Ace Thread
50 Ace Thread
25 cm
Porous Glass Frit
O-Rings
10 cm
7 Ace Thread

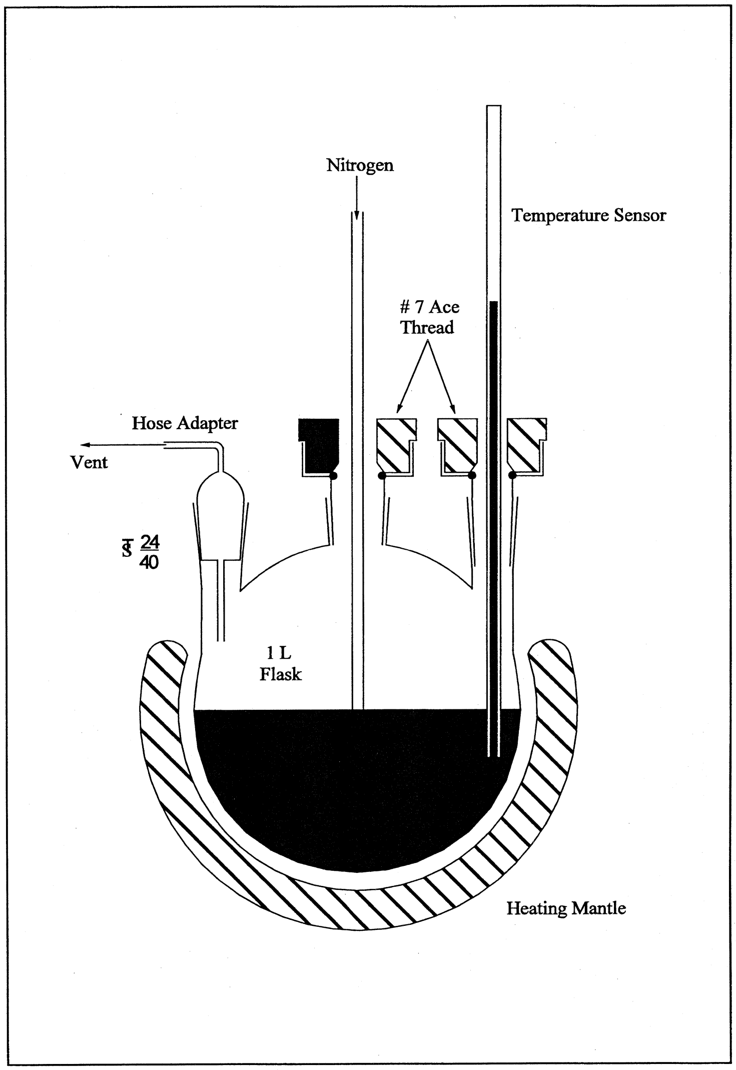


Figure 25D-4. Schematic of PEG Cleaning System.

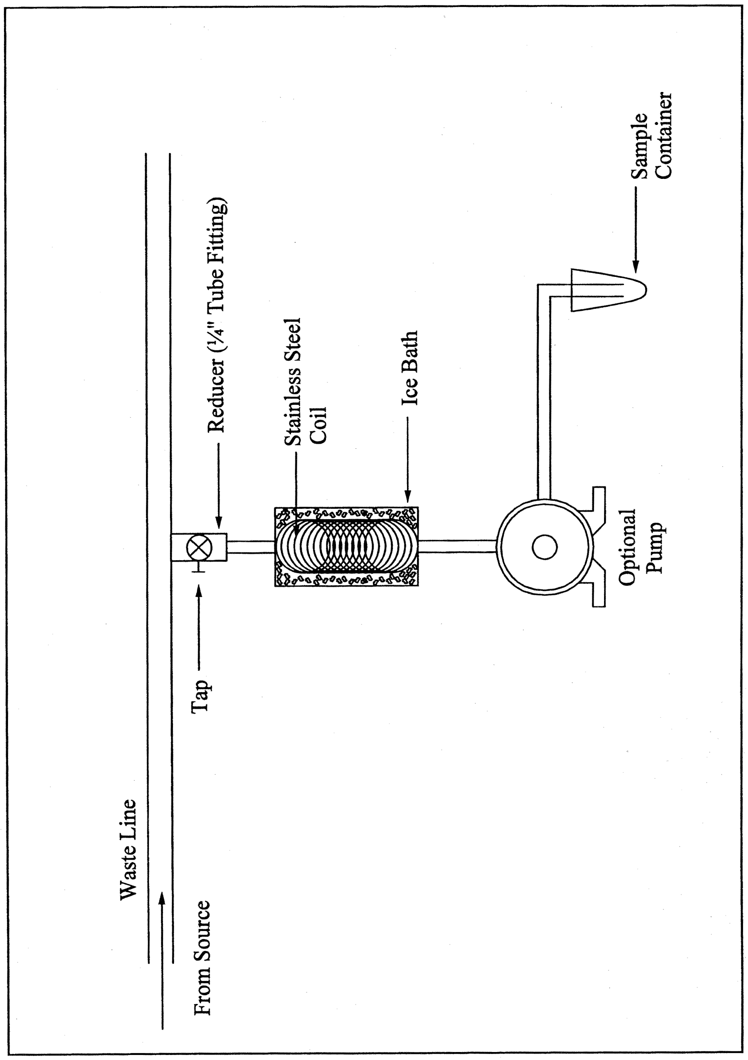


Figure 25D-5. Schematic of Sampling Apparatus.

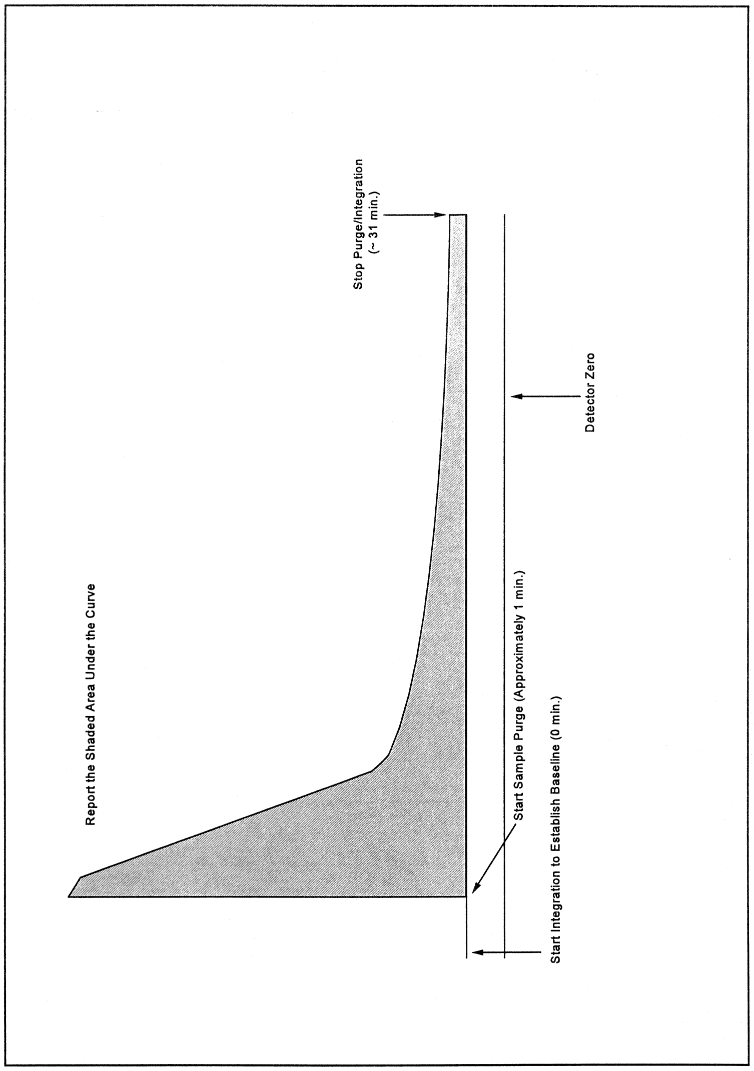


Figure 25D-6. Example Integration of Either Detector.

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.

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 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_a = Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.
C_m = 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_{bar} = 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.
$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], (4.91×10^{-7} psi/[(in. Hg)(ppm)])

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

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

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.

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

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

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

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.

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

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

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

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

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

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

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.

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

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

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

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.

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

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

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

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

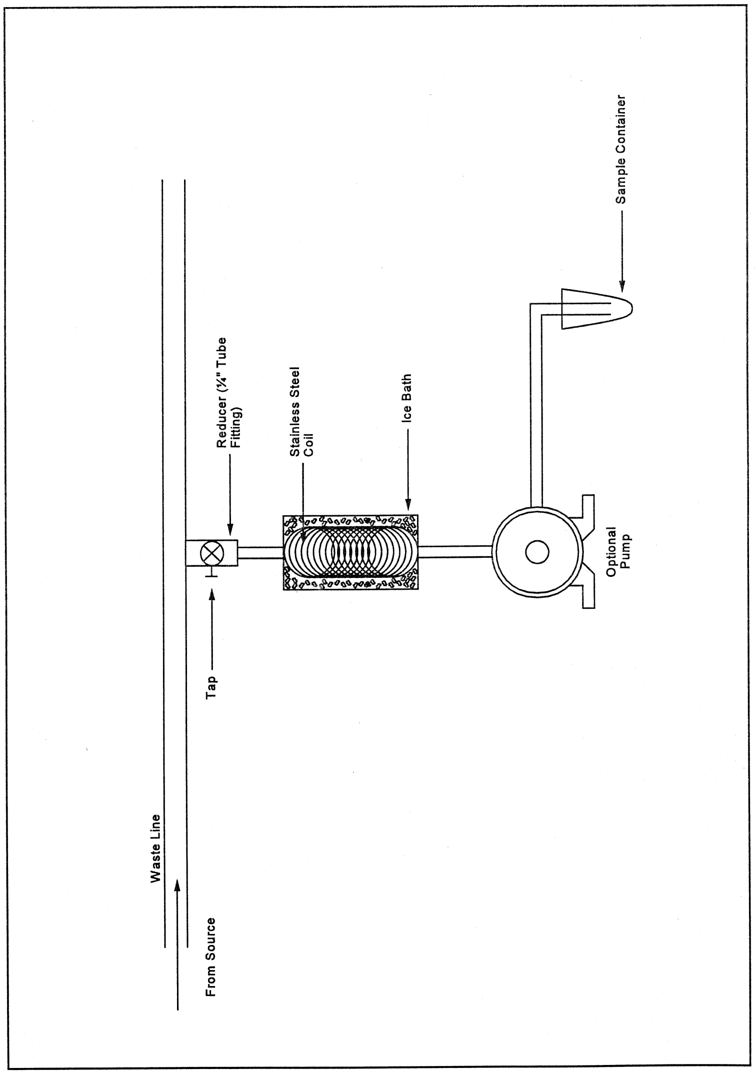


Figure 25E-1. Schematic of Sampling Apparatus

[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

Method 27—Determination of vapor tightness of gasoline delivery tank using pressure-vacuum test
Method 28—Certification and auditing of wood heaters
Method 28A—Measurement of air to fuel ratio and minimum achievable burn rates for wood-fired appliances
Method 29—Determination of metals emissions from stationary sources

The test methods in this appendix are referred to in § 60.8 (Performance Tests) and § 60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title ''Test Methods and Procedures'' is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as ''subject to the approval of the Administrator'' or as ''or equivalent.'' Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

METHOD 26—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES NON-ISOKINETIC METHOD

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) (HCl, HBr, and HF) and halogens (X_2) (Cl_2 and Br_2) from stationary sources when specified by the applicable subpart. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

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 An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of HBr and CL_2 may cause a positive bias in the HCL result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^- to interfere with measurements of very low Br^- levels.

4.4 A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result.

4.5 There is anecdotal evidence that HF may be outgassed from new teflon components. If HF is a target analyte, then preconditioning of new teflon components, by heating should be considered.

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 to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

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 sampling train is shown in Figure 26–1, and component parts are discussed below.

6.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system capable of maintaining a probe gas temperature during sampling between 120 and 134 °C (248 and 273 °F) to prevent moisture condensation; or Teflon where stack probes are below 210 °C. If HF is a target analyte, then preconditioning of new teflon components by heating should be considered to prevent potential HF outgassing. A Teflon-glass filter in a mat configuration should be installed to remove particulate matter from the gas stream.

6.1.2 Three-way Stopcock. A borosilicate-glass three-way stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect to the outlet of the heated filter and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

6.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

6.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.1.5 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 and 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.6 Filter Holder and Support. The filter holder shall be made of Teflon or quartz. The filter support shall be made of Teflon. All Teflon filter holders and supports are available from Savillex Corp., 5325 Hwy 101, Minnetonka, MN 55345.

6.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

6.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min (0.07 ft^3/min).

6.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min (0.2 ft^3/min).

6.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, sections 6.1.1.4, 6.1.1.7, 6.1.1.8, 6.1.1.10, 6.1.2, and 6.1.3.

6.1.11 Temperature Measuring Devices. Temperature sensors to monitor the temperature of the probe and to monitor the temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

6.1.12 Ice Water Bath. To minimize loss of absorbing solution.

6.2 Sample Recovery.

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

6.2.2 Storage Bottles. 100- or 250-ml, high-density polyethylene bottles with Teflon screw cap liners to store impinger samples.

6.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

6.3.1 Volumetric Flasks. Class A, 100-ml size.

6.3.2 Volumetric Pipets. Class A, assortment. To dilute samples to the calibration range of the ion chromatograph.

6.3.3 Ion Chromatograph (IC). Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. A 25-mm (1 in) (or other size) Teflon glass mat, Pallflex TX40HI75 (Pallflex Inc., 125 Kennedy Drive, Putnam, CT 06260). This filter is in a mat configuration to prevent fine particulate matter from entering the sampling train. Its composition is 75% Teflon/25% borosilicate glass. Other filters may be used, but they must be in a mat (as opposed to a laminate) configuration and contain at least 75% Teflon. For practical rather than scientific reasons, when the stack gas temperature exceeds 210 °C (410 °F) and the HCl concentration is greater than 20 ppm, a quartz-fiber filter may be used since Teflon becomes unstable above this temperature.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

7.1.4 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 180 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.1.5 Alkaline Adsorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the third and fourth impinger, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final solution volume to 100 ml using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate ($Na_2S_2O_3$ 5 H_2O)

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26–2 and 26–3 in section 12.2, to calculate the Br^- and F^- concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin-or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the ''water dip'' resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analyst should be trained and experienced with the procedure to ensure reliable results.

8.1 Sampling.

8.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

8.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock (*i.e.*, the heated area in Figure 26–1) to a temperature sufficient to prevent water condensation. This temperature must be maintained between 120 and 134 °C (248 and 273 °F). The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained. It is important to maintain a temperature around the probe and filter in this range since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and, hence, any collection of acid gases on these components would result in potential undereporting of these emissions. The applicable subparts may specify alternative higher temperatures.)

8.1.3 Leak-Check Procedure.

8.1.3.1 Sampling Train. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable [*e.g.*, 0–40 cc/min (0–2.4 in^3/min)] rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3.2 Pump. It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in) Hg, plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

8.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26–1). Turn on the purge pump, and adjust the purge rate to 2 liters/min (0.07 ft^3/min). Purge for at least 5 minutes before sampling.

8.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 26–1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in section 8.1.3.1.

8.2 Sample Recovery.

8.2.1 Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle.

8.2.2 Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle. Add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg per ppm-dscf).

NOTE: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.3 Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in section 7.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, prelabeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

8.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Volume Metering System, Temperature Sensors, Rate Meter, and Barometer. Same as in Method 6, sections 10.1, 10.2, 10.3, and 10.4.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or heights, for the standards and plot individual values versus halide ion concentrations in μg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 μl sample loop, and a conductivity detector set on 1.0 μS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicate injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature.

B_{X^-} = Mass concentration of applicable absorbing solution blank, μg halide ion (Cl^-, Br^-, F^-) /ml, not to exceed 1 μg/ml which is 10 times the published analytical detection limit of 0.1 μg/ml.
C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.
K = 10^{-3} mg/μg.
K_{HCl} = 1.028 (μg HCl/μg-mole)/(μg Cl^-/μg-mole).
K_{HBr} = 1.013 (μg HBr/μg-mole)/(μg Br^-/μg-mole).
K_{HF} = 1.053 (μg HF/μg-mole)/(μg F^-/μg-mole).
m_{HX} = Mass of HCl, HBr, or HF in sample, μg.
m_{X2} = Mass of Cl_2 or Br_2 in sample, μg.
S_{X^-} = Analysis of sample, μg halide ion (Cl^-, Br^-, F^-)/ml.
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.
V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26-3}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6–1 of Method 6.

12.4 Total μg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HCl,Hbr,HF} V_s \left(S_x{}^- - B_x{}^-\right) \qquad \text{Eq. 26-4}$$

12.5 Total μg Cl_2 or Br_2 Per Sample.

$$M_{x2} = V_s \left(S_X{}^- - B_X{}^-\right) \qquad \text{Eq. 26-5}$$

12.6 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K m_{XH,X2}/V_{m(std)} \qquad \text{Eq. 26-6}$$

13.0 Method Performance

13.1 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit a bias to Cl_2 when sampling at concentrations less than 50 ppm.

13.2 Sample Stability. The collected Cl^- samples can be stored for up to 4 weeks.

13.3 Detection Limit. A typical IC instrumental detection limit for Cl^- is 0.2 µg/ml. Detection limits for the other analyses should be similar. Assuming 50 ml liquid recovered from both the acidified impingers, and the basic impingers, and 0.12 dscm (4.24 dscf) of stack gas sampled, then the analytical detection limit in the stack gas would be about 0.05 ppm for HCl and Cl_2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

Method 26A. Method 26A, which uses isokinetic sampling equipment, is an acceptable alternative to Method 26.

17.0 References

1. Steinsberger, S. C. and J. H. Margeson, ‘‘Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators,’’ U.S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3–89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California, Air Resources Board, Method 421, ‘‘Determination of Hydrochloric Acid Emissions from Stationary Sources,’’ March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D. A., B. M. Myatt, J. F. Lachowski, and K. T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R. D. and S. A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

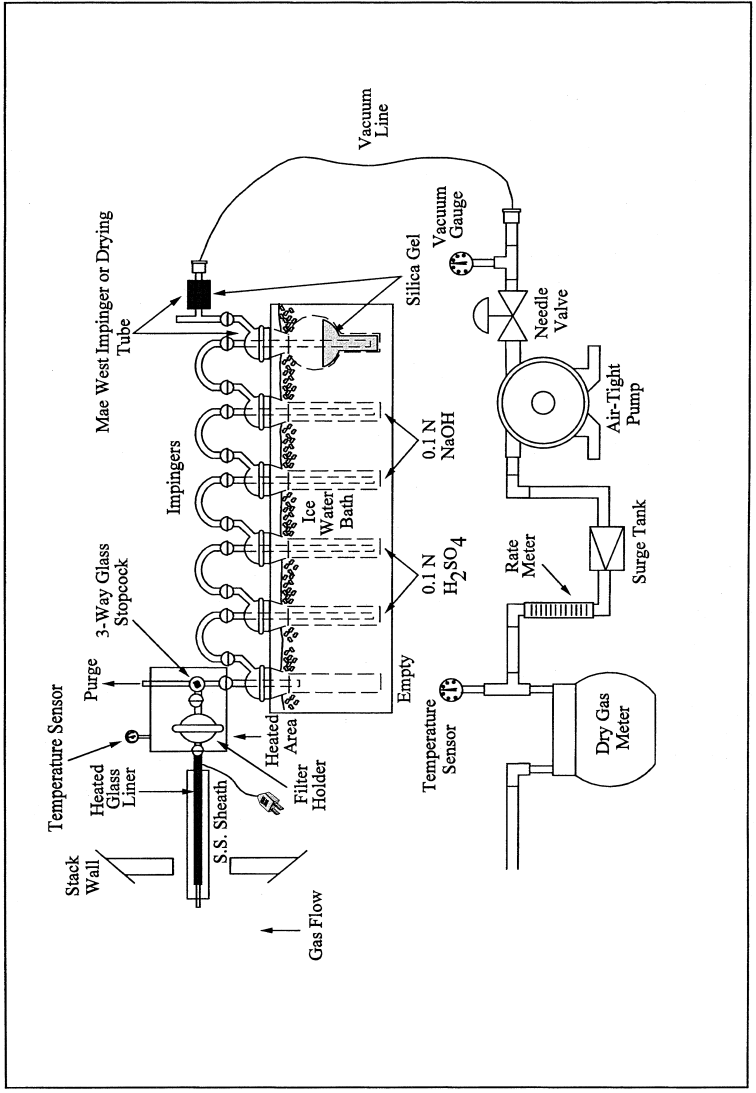


Figure 26-1. Sampling Train.

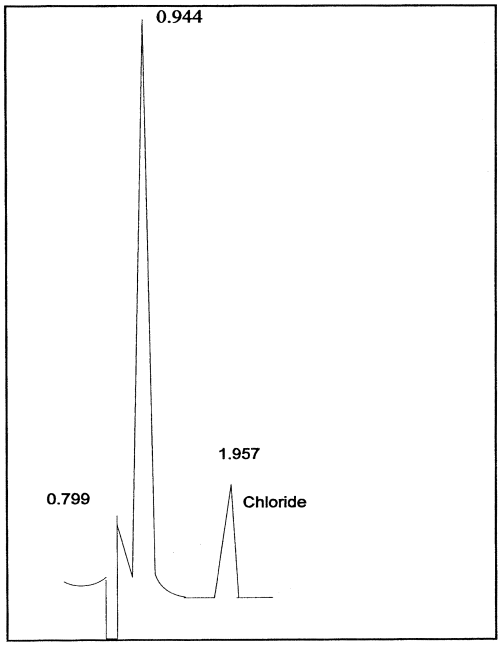


Figure 26-2. Example Chromatogram.

METHOD 26A—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD

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 have a thorough knowledge of at least the following additional test methods: Method 2, Method 5, and Method 26.

1.0 Scope and Application

1.1 Analytes.

Analytes	CAS No.
Hydrogen Chloride (HCl)	7647–01–0
Hydrogen Bromide (HBr)	10035–10–6
Hydrogen Fluoride (HF)	7664–39–3
Chlorine (Cl_2)	7882–50–5
Bromine (Br_2)	7726–95–6

1.2 This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X_2) [Cl_2 and Br_2] from stationary sources when specified by the applicable subpart. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (*e.g.*, hydrogen halides dissolved in water droplets).

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 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any liquid present. The filter collects particulate matter including halide salts but is not routinely recovered or analyzed. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

NOTE: If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon probe liner, cyclone, and filter holder should not be used. The Teflon filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hypohalous acid upon dissolution in water. The use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution.

4.2 The simultaneous presence of both HBr and Cl_2 may cause a positive bias in the HCl result with a corresponding negative bias in the Cl_2 result as well as affecting the HBr/Br_2 split.

4.3 High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^- levels. Dissociating chloride salts (*e.g.*, ammonium chloride) at elevated temperatures interfere with halogen acid measurement in this method. Maintaining particulate probe/filter temperatures between 120 °C and 134 °C (248 °F and 273 °F) minimizes this interference.

4.4 There is anecdotal evidence that HF may be outgassed from new Teflon components. If HF is a target analyte then preconditioning of new Teflon components, by heating, should be considered.

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 to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

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 sampling train is shown in Figure 26A–1; the apparatus is similar to the Method 5 train where noted as follows:

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5, sections 6.1.1.1 and 10.1, and coupled to the probe liner using a Teflon union; a stainless steel nut is recommended for this union. When the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used.

6.1.2 Probe Liner. Same as Method 5, section 6.1.1.2, except metal liners shall not be used. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500 °C (932 °F). Teflon may be used in limited applications where the minimum stack temperature exceeds 120 °C (250 °F) but never exceeds the temperature where Teflon is estimated to become unstable [approximately 210 °C (410 °F)].

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.9, 6.1.2, and 6.1.3.

6.1.4 Cyclone (Optional). Glass or Teflon. Use of the cyclone is required only when the sample gas stream is saturated with moisture; however, the cyclone is recommended to protect the filter from any liquid droplets present.

6.1.5 Filter Holder. Borosilicate or quartz glass, or Teflon filter holder, with a Teflon filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

6.1.6 Impinger Train. The following system shall be used to determine the stack gas moisture content and to collect the hydrogen halides and halogens: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. The first impinger shown in Figure 26A–1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under high moisture conditions. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.1 N H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (Method 5, section 6.1.1.8). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) shall be of the modified Greenburg-Smith design (Method 5, section 6.1.1.8). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant. Teflon impingers are an acceptable alternative.

6.1.7 Heating System. Any heating system capable of maintaining a temperature around the probe and filter holder between 120 and 134 °C (248 to 273 °F) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application.

6.1.8 Ambient Air Conditioning Tube (Optional). Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh sodium hydroxide-coated silica, or equivalent, (Ascarite II has been found suitable) to dry and remove acid gases from the ambient air used to remove moisture from the filter and cyclone, when the cyclone is used. The inlet and outlet ends of the tube should be packed with at least 1-cm thickness of glass wool or filter material suitable to prevent escape of fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle following the test run.

6.2 Sample Recovery.

6.2.1 Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Glass Sample Storage Containers, Petri Dishes, Graduated Cylinder and/or Balance, and Rubber Policeman. Same as Method 5, sections 6.2.1, 6.2.2, 6.2.3, 6.2.4, 6.2.5, and 6.2.7.

6.2.2 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel. High-density polyethylene bottles with Teflon screw cap liners to store impinger reagents, 1-liter.

6.2.3 Funnels. Glass or high-density polyethylene, to aid in sample recovery.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks. Class A, various sizes.

6.3.2 Volumetric Pipettes. Class A, assortment. To dilute samples to calibration range of the ion chromatograph (IC).

6.3.3 Ion Chromatograph (IC). Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

7.1 Sampling.

7.1.1 Filter. Teflon mat (*e.g.*, Pallflex TX40HI45) filter. When the stack gas temperature exceeds 210 °C (410 °F) a quartz fiber filter may be used.

7.1.2 Water. Deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193–77 or 91, Type 3 (incorporated by reference—see §60.17).

7.1.3 Acidic Absorbing Solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 1 L, slowly add 2.80 ml of concentrated 17.9 M H2SO4 to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.4 Silica Gel, Crushed Ice, and Stopcock Grease. Same as Method 5, sections 7.1.2, 7.1.4, and 7.1.5, respectively.

7.1.5 Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume to 1 L using additional water. Shake well to mix the solution.

7.1.6 Sodium Thiosulfate, ($Na_2S_2O_33.5\ H_2O$).

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 200 ml of each absorbing solution (250 ml of the acidic absorbing solution, if a condensate impinger is used) to the same final volume as the field samples using the blank sample of rinse water. If a particulate determination is conducted, collect a blank sample of acetone.

7.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110 °C (230 °F) for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^-concentration using Equation 26A–1 in section 12.2. In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26A–2 and 26A–3 in section 12.2, to calculate the $Br^-$and F^-concentrations. Alternately, solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

7.2.4 Chromatographic Eluent. Same as Method 26, section 7.2.4.

7.2.5 Water. Same as section 7.1.1.

7.2.6 Acetone. Same as Method 5, section 7.2.

8.0 Sample Collection, Preservation, Storage, and Transport

NOTE: Because of the complexity of this method, testers and analysts should be trained and experienced with the procedures to ensure reliable results.

8.1 Sampling.

8.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 8.1, except the filter need only be desiccated and weighed if a particulate determination will be conducted.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.1.3 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 8.1.3, except for the following variations: Add 50 ml of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 ml of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200–300 g of preweighed silica gel from its container to the last impinger. Set up the train as in Figure 26A–1. When used, the optional cyclone is inserted between the probe liner and filter holder and located in the heated filter box.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, sections 8.4.2 (Pretest Leak-Check), 8.4.3 (Leak-Checks During the Sample Run), and 8.4.4 (Post-Test Leak-Check).

8.1.5 Sampling Train Operation. Follow the general procedure given in Method 5, Section 8.5. It is important to maintain a temperature around the probe, filter (and cyclone, if used) between 120 and 134 °C (248 and 273 °F) since it is extremely difficult to purge acid gases off these components. (These components are not quantitatively recovered and hence any collection of acid gases on these components would result in potential undereporting these emissions. The applicable subparts may specify alternative higher temperatures.) For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5–3. If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N H2SO4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. Before the sampling train integrity is compromised by removing the impinger, conduct a leak-check as described in Method 5, Section 8.4.2.

8.1.6 Post-Test Moisture Removal (Optional). When the optional cyclone is included in the sampling train or when liquid is visible on the filter at the end of a sample run even in the absence of a cyclone, perform the following procedure. Upon completion of the test run, connect the ambient air conditioning tube at the probe inlet and operate the train with the filter heating system between 120 and 134 °C (248 and 273 °F) at a low flow rate (*e.g.*, $\Delta H = 1$ in. H_2O) to vaporize any liquid and hydrogen halides in the cyclone or on the filter and pull them through the train into the impingers. After 30 minutes, turn off the flow, remove the conditioning tube, and examine the cyclone and filter for any visible liquid. If liquid is visible, repeat this step for 15 minutes and observe again. Keep repeating until the cyclone is dry.

NOTE: It is critical that this procedure is repeated until the cyclone is completely dry.

8.2 Sample Recovery. Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap loosely over the tip to prevent gaining or losing particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder. Before moving the sampling train to the cleanup site, remove the probe from the sample train, wipe off any silicone grease, and cap the open outlet of the impinger train, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm, or aluminum foil may be used to close these openings. Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss. Inspect the train prior to and during disassembly and note any abnormal conditions. Treat samples as follows:

8.2.1 Container No. 1 (Optional; Filter Catch for Particulate Determination). Same as Method 5, section 8.7.6.1, Container No. 1.

8.2.2 Container No. 2 (Optional; Front-Half Rinse for Particulate Determination). Same as Method 5, section 8.7.6.2, Container No. 2.

8.2.3 Container No. 3 (Knockout and Acid Impinger Catch for Moisture and Hydrogen Halide Determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to ±1 ml by using a graduated cylinder or by weighing it to ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and connecting glassware including the back portion of the filter holder (and flexible tubing, if used) with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks to be analyzed with the samples.

8.2.4 Container No. 4 (Alkaline Impinger Catch for Halogen and Moisture Determination). Measure and record the liquid in the alkaline impingers as described in section 8.2.3. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 25 mg of sodium thiosulfate per ppm halogen anticipated to be in the stack gas multiplied by the volume (dscm) of stack gas sampled (0.7 mg/ppm-dscf). Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank to be analyzed with the samples.

NOTE: 25 mg per sodium thiosulfate per ppm halogen anticipated to be in the stack includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl^- ion in the alkaline solution.

8.2.5 Container No. 5 (Silica Gel for Moisture Determination). Same as Method 5, section 8.7.6.3, Container No. 3.

8.2.6 Container Nos. 6 through 9 (Reagent Blanks). Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train; dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same ratio of sodium thiosulfate solution used in container No. 4 to the 0.1 N NaOH absorbing reagent blank. Also, save a portion of the rinse water alone and a portion of the acetone equivalent to the amount used to rinse the front half of the sampling train. Place each in a separate, prelabeled sample container.

8.2.7 Prior to shipment, recheck all sample containers to ensure that the caps are well-secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1.4, 10.1	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak-Check of Metering System, and Barometer. Same as Method 5, sections 10.1, 10.2, 10.3, 10.4, 10.5, 8.4.1, and 10.6, respectively.

10.2 Ion Chromatograph.

10.2.1 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_4 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the three stock solutions such that they are within the linear range of the field samples.

10.2.2 Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest.

10.2.3 Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis. The values from duplicate injections of these calibration samples should agree within 5 percent of their mean for the analysis to be valid.

10.2.4 Determine the peak areas, or height, of the standards and plot individual values versus halide ion concentrations in μg/ml.

10.2.5 Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

11.0 Analytical Procedures

NOTE: The liquid levels in the sample containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.1 Sample Analysis.

11.1.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 μl sample loop, and a conductivity detector set on 1.0 μS full scale is shown in Figure 26–2.

11.1.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to section 10.2. Ensure adequate baseline separation of the analyses.

11.1.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. If the values of duplicate injections are not within 5 percent of the mean, the duplicator injections shall be repeated and all four values used to determine the average response. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2 Container Nos. 1 and 2 and Acetone Blank (Optional; Particulate Determination). Same as Method 5, sections 11.2.1 and 11.2.2, respectively.

11.3 Container No. 5. Same as Method 5, section 11.2.3 for silica gel.

12.0 Data Analysis and Calculations

NOTE: Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

12.1 Nomenclature. Same as Method 5, section 12.1. In addition:

B_{X^-} = Mass concentration of applicable absorbing solution blank, μg halide ion (Cl^-, Br^-, F^-)/ml, not to exceed 1 μg/ml which is 10 times the published analytical detection limit of 0.1 μg/ml. (It is also approximately 5 percent of the mass concentration anticipated to result from a one hour sample at 10 ppmv HCl.)

C = Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

K = 10^{-3} mg/μg.

K_{HCl} = 1.028 (μg HCl/μg-mole)/(μg Cl^-/μg-mole).

K_{HBr} = 1.013 (μg HBr/μg-mole)/(μg Br^-/μg-mole).

K_{HF} = 1.053 (μg HF/μg-mole)/(μg F^-/μg-mole).

m_{HX} = Mass of HCl, HBr, or HF in sample, ug.

m_{X2} = Mass of Cl_2 or Br_2 in sample, ug.

S_{X^-} = Analysis of sample, ug halide ion (Cl^-, Br^-, F^-)/ml.

V_s = Volume of filtered and diluted sample, ml.

12.2 Calculate the exact Cl^-, Br^-, and F^- concentration in the halide salt stock standard solutions using the following equations.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \qquad \text{Eq. 26A-1}$$

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \qquad \text{Eq. 26A-2}$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \qquad \text{Eq. 26A-3}$$

12.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5–3 of Method 5).

12.4 Dry Gas Volume. Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in section 12.3 of Method 5.

12.5 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor $V_{w(std)}$ and moisture content B_{ws} from the data obtained in this method (Figure 5–3 of Method 5); use Equations 5–2 and 5–3 of Method 5.

12.6 Isokinetic Variation and Acceptable Results. Use Method 5, section 12.11.

12.7 Acetone Blank Concentration, Acetone Wash Blank Residue Weight, Particulate Weight, and Particulate Concentration. For particulate determination.

12.8 Total μg HCl, HBr, or HF Per Sample.

$$m_{HX} = K_{HCl,Hbr,HF} V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-4}$$

12.9 Total μg Cl_2 or Br_2 Per Sample.

$$m_{X2} = V_s \left(S_{X^-} - B_{X^-} \right) \qquad \text{Eq. 26A-5}$$

12.10 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$$C = K\, m_{HX,X2} / V_{m(std)} \qquad \text{Eq. 26A-6}$$

12.11 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.3 and 12.4 of Method 2.

13.0 Method Performance

13.1 Precision and Bias. The method has a possible measurable negative bias below 20 ppm HCl perhaps due to reaction with small amounts of moisture in the probe and filter. Similar bias for the other hydrogen halides is possible.

13.2 Sample Stability. The collected Cl- samples can be stored for up to 4 weeks for analysis for HCl and Cl2.

13.3 Detection Limit. A typical analytical detection limit for HCl is 0.2 μg/ml. Detection limits for the other analyses should be similar. Assuming 300 ml of liquid recovered for the acidified impingers and a similar amounts recovered from the basic impingers, and 1 dscm of stack gas sampled, the analytical detection limits in the stack gas would be about 0.04 ppm for HCl and Cl2, respectively.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Steinsberger, S. C. and J. H. Margeson. Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators. U.S. Environmental Protection Agency, Office of Research and Development. Publication No. 600/3–89/064. April 1989. Available from National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California Air Resources Board. Method 421—Determination of Hydrochloric Acid Emissions from Stationary Sources. March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emissions. J. Environ. Sci. Health. *A19*(3): 337–350. 1984.

4. Stern, D.A., B.M. Myatt, J.F. Lachowski, and K.T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2–4, 1983. Publication No. 600/9–84–015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84–234525.

5. Holm, R.D. and S.A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J.D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99–110.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

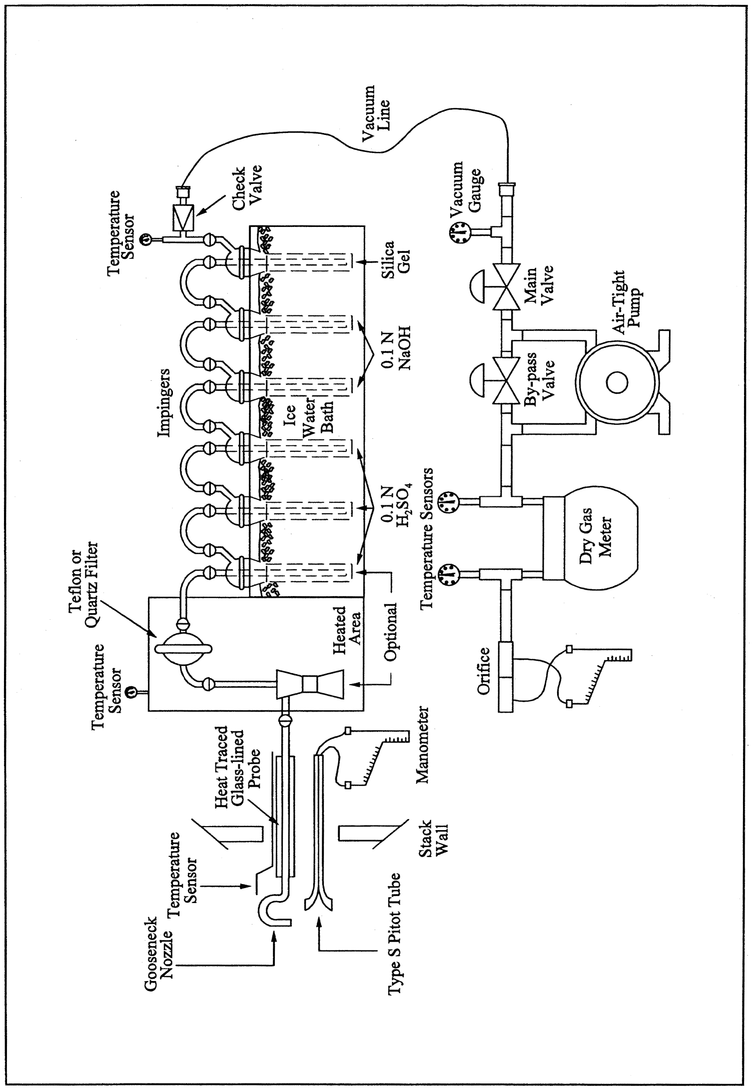


Figure 26A-1. Sampling Train

METHOD 27—DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE DELIVERY TANK USING PRESSURE VACUUM TEST

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery collection equipment.

2.0 Summary of Method

2.1 Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

3.0 Definitions

3.1 *Allowable pressure change (Δp)* means the allowable amount of decrease in pressure during the static pressure test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.2 *Allowable vacuum change (Δv)* means the allowable amount of decrease in vacuum during the static vacuum test, within the time period t, as specified in the appropriate regulation, in mm H_2O.

3.3 *Compartment* means a liquid-tight division of a delivery tank.

3.4 *Delivery tank* means a container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

3.5 *Delivery tank vapor collection equipment* means any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

3.6 *Gasoline* means a petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

3.7 *Initial pressure (P_i)* means the pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H_2O.

3.8 *Initial vacuum (V_i)* means the vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H_3.

3.9 *Time period of the pressure or vacuum test (t)* means the time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Gasoline contains several volatile organic compounds (*e.g.*, benzene and hexane) which presents a potential for fire and/or explosions. It is advisable to take appropriate precautions when testing a gasoline vessel's vapor tightness, such as refraining from smoking and using explosion-proof equipment.

5.2 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

6.0 Equipment and Supplies

The following equipment and supplies are required for testing:

6.1 Pressure Source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm (20 in.) H_2O above atmospheric pressure.

6.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

6.3 Vacuum Source. Vacuum pump capable of evacuating the delivery tank to 250 mm (10 in.) H_2O below atmospheric pressure.

6.4 Pressure-Vacuum Supply Hose.

6.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm (20 in.) H_2O gauge pressure with ±2.5 mm (0.1 in.) H_2O precision.

6.6 Pressure-Vacuum Relief Valves. The test apparatus shall be equipped with an inline pressure-vacuum relief valve set to activate at 675 mm (26.6 in.) H_2O above atmospheric pressure or 250 mm (10 in.) H2O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

6.7 Test Cap for Vapor Recovery Hose. This cap shall have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure-vacuum supply hose.

6.8 Caps for Liquid Delivery Hoses.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparations.

8.1.1 Summary. Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to completely attain these pretest conditions, a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criteria in sections 8.2.2.5 and 8.2.3.5.

8.1.2 Emptying of Tank. The delivery tank shall be emptied of all liquid.

8.1.3 Purging of Vapor. As much as possible the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a much longer time for stabilization during the testing.

8.1.4 Temperature Stabilization. As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

8.2 Test Procedure.

8.2.1 Preparations.

8.2.1.1 Open and close each dome cover.

8.2.1.2 Connect static electrical ground connections to the tank. Attach the liquid delivery and vapor return hoses, remove the liquid delivery elbows, and plug the liquid delivery fittings.

NOTE: The purpose of testing the liquid delivery hoses is to detect tears or holes that would allow liquid leakage during a delivery. Liquid delivery hoses are not considered to be possible sources of vapor leakage, and thus, do not have to be attached for a vapor leakage test. Instead, a liquid delivery hose could be either visually inspected, or filled with water to detect any liquid leakage.

8.2.1.3 Attach the test cap to the end of the vapor recovery hose.

8.2.1.4 Connect the pressure-vacuum supply hose and the pressure-vacuum relief valve to the shut-off valve. Attach a manometer to the pressure tap.

8.2.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately, as if it were an individual delivery tank.

8.2.2 Pressure Test.

8.2.2.1 Connect the pressure source to the pressure-vacuum supply hose.

8.2.2.2 Open the shut-off valve in the vapor recovery hose cap. Apply air pressure slowly, pressurize the tank to P_i, the initial pressure specified in the regulation.

8.2.2.3 Close the shut-off and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of P_i. When the pressure stabilizes, record the time and initial pressure.

8.2.2.4 At the end of the time period (t) specified in the regulation, record the time and final pressure.

8.2.2.5 Repeat steps 8.2.2.2 through 8.2.2.4 until the change in pressure for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.2.6 Compare the average measured change in pressure to the allowable pressure change, Δp, specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

8.2.2.7 Disconnect the pressure source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.3 Vacuum Test.

8.2.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

8.2.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to V_i, the initial vacuum specified in the regulation.

8.2.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of V_i. When the pressure stabilizes, record the time and initial vacuum.

8.2.3.4 At the end of the time period specified in the regulation (t), record the time and final vacuum.

8.2.3.5 Repeat steps 8.2.3.2 through 8.2.3.4 until the change in vacuum for two consecutive runs agrees within 12.5 mm (0.5 in.) H_2O. Calculate the arithmetic average of the two results.

8.2.3.6 Compare the average measured change in vacuum to the allowable vacuum change, Δv, as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

8.2.3.7 Disconnect the vacuum source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

8.2.4 Post-Test Clean-up. Disconnect all test equipment and return the delivery tank to its pretest condition.

9.0 Quality Control

Section(s)	Quality control measure	Effect
8.2.2.5, 8.3.3.5	Repeat test procedures until change in pressure or vacuum for two consecutive runs agrees within ±12.5 mm (0.5 in.) H_2O.	Ensures data precision.

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations [Reserved]

13.0 Method Performance

13.1 Precision. The vapor tightness of a gasoline delivery tank under positive or negative pressure, as measured by this method, is precise within 12.5 mm (0.5 in.) H_2O

13.2 Bias. No bias has been identified.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 The pumping of water into the bottom of a delivery tank is an acceptable alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

16.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

17.0 References [Reserved]

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

METHOD 28—CERTIFICATION AND AUDITING OF WOOD HEATERS

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 have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 4, Method 5, Method 5G, Method 5H, Method 6, Method 6C, and Method 16A.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the certification and auditing of wood heaters, including pellet burning wood heaters.

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 Particulate matter emissions are measured from a wood heater burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates and particulate emission rates and for reducing data are provided.

3.0 Definitions

3.1 *2 × 4 or 4 × 4* means two inches by four inches or four inches by four inches (50 mm by 100 mm or 100 mm by 100 mm), as nominal dimensions for lumber.

3.2 *Burn rate* means the rate at which test fuel is consumed in a wood heater. Measured in kilograms or lbs of wood (dry basis) per hour (kg/hr or lb/hr).

3.3 *Certification or audit test* means a series of at least four test runs conducted for certification or audit purposes that meets the burn rate specifications in section 8.4.

3.4 *Firebox* means the chamber in the wood heater in which the test fuel charge is placed and combusted.

3.5 *Height* means the vertical distance extending above the loading door, if fuel could reasonably occupy that space, but not more than 2 inches above the top (peak height) of the loading door, to the floor of the firebox (*i.e.*, below a permanent grate) if the grate allows a 1-inch diameter piece of wood to pass through the grate, or, if not, to the top of the grate. Firebox height is not necessarily uniform but must account for variations caused by internal baffles, air channels, or other permanent obstructions.

3.6 *Length* means the longest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.7 *Pellet burning wood heater* means a wood heater which meets the following criteria: (1) The manufacturer makes no reference to burning cord wood in advertising or other literature, (2) the unit is safety listed for pellet fuel only, (3) the unit operating and instruction manual must state that the use of cordwood is prohibited by law, and (4) the unit must be manufactured and sold including the hopper and auger combination as integral parts.

3.8 *Secondary air supply* means an air supply that introduces air to the wood heater such that the burn rate is not altered by more than 25 percent when the secondary air supply is adjusted during the test run. The wood heater manufacturer can document this through design drawings that show the secondary air is introduced only into a mixing chamber or secondary chamber outside the firebox.

3.9 *Test facility* means the area in which the wood heater is installed, operated, and sampled for emissions.

3.10 *Test fuel charge* means the collection of test fuel pieces placed in the wood heater at the start of the emission test run.

3.11 *Test fuel crib* means the arrangement of the test fuel charge with the proper spacing requirements between adjacent fuel pieces.

3.12 *Test fuel loading density* means the weight of the as-fired test fuel charge per unit volume of usable firebox.

3.13 *Test fuel piece* means the 2 × 4 or 4 × 4 wood piece cut to the length required for the test fuel charge and used to construct the test fuel crib.

3.14 *Test run* means an individual emission test which encompasses the time required to consume the mass of the test fuel charge.

3.15 *Usable firebox volume* means the volume of the firebox determined using its height, length, and width as defined in this section.

3.16 *Width* means the shortest horizontal fire chamber dimension that is parallel to a wall of the chamber.

3.17 *Wood heater* means an enclosed, woodburning appliance capable of and intended for space heating or domestic water heating, as defined in the applicable regulation.

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

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

6.1 Insulated Solid Pack Chimney. For installation of wood heaters. Solid pack insulated chimneys shall have a minimum of 2.5 cm (1 in.) solid pack insulating material surrounding the entire flue and possess a label demonstrating conformance to U.L. 103 (incorporated by reference—see § 60.17).

6.2 Platform Scale and Monitor. For monitoring of fuel load weight change. The scale shall be capable of measuring weight to within 0.05 kg (0.1 lb) or 1 percent of the initial test fuel charge weight, whichever is greater.

6.3 Wood Heater Temperature Monitors. Seven, each capable of measuring temperature to within 1.5 percent of expected absolute temperatures.

6.4 Test Facility Temperature Monitor. A thermocouple located centrally in a vertically oriented 150 mm (6 in.) long, 50 mm (2 in.) diameter pipe shield that is open at both ends, capable of measuring temperature to within 1.5 percent of expected temperatures.

6.5 Balance (optional). Balance capable of weighing the test fuel charge to within 0.05 kg (0.1 lb).

6.6 Moisture Meter. Calibrated electrical resistance meter for measuring test fuel moisture to within 1 percent moisture content.

6.7 Anemometer. Device capable of detecting air velocities less than 0.10 m/sec (20 ft/min), for measuring air velocities near the test appliance.

6.8 Barometer. Mercury, aneroid or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

6.9 Draft Gauge. Electromanometer or other device for the determination of flue draft or static pressure readable to within 0.50 Pa (0.002 in. H_2O).

6.10 Humidity Gauge. Psychrometer or hygrometer for measuring room humidity.

6.11 Wood Heater Flue.

6.11.1 Steel flue pipe extending to 2.6 ±0.15 m (8.5 ±0.5 ft) above the top of the platform scale, and above this level, insulated solid pack type chimney extending to 4.6 ±0.3 m (15 ±1 ft) above the platform scale, and of the size specified by the wood heater manufacturer. This applies to both freestanding and insert type wood heaters.

6.11.2 Other chimney types (*e.g.*, solid pack insulated pipe) may be used in place of the steel flue pipe if the wood heater manufacturer's written appliance specifications require such chimney for home installation (*e.g.*, zero clearance wood heater inserts). Such alternative chimney or flue pipe must remain and be sealed with the wood heater following the certification test.

6.12 Test Facility. The test facility shall meet the following requirements during testing:

6.12.1 The test facility temperature shall be maintained between 18 and 32 °C (65 and 90 °F) during each test run.

6.12.2 Air velocities within 0.6 m (2 ft) of the test appliance and exhaust system shall be less than 0.25 m/sec (50 ft/min) without fire in the unit.

6.12.3 The flue shall discharge into the same space or into a space freely communicating with the test facility. Any hood or similar device used to vent combustion products shall not induce a draft greater than 1.25 Pa (0.005 in. H_2O) on the wood heater measured when the wood heater is not operating.

6.12.4 For test facilities with artificially induced barometric pressures (*e.g.*, pressurized chambers), the barometric pressure in the test facility shall not exceed 775 mm Hg (30.5 in. Hg) during any test run.

7.0 Reagents and Standards

Same as section 6.0 of either Method 5G or Method 5H, with the addition of the following:

7.1 Test Fuel. The test fuel shall conform to the following requirements:

7.1.1 Fuel Species. Untreated, air-dried, Douglas fir lumber. Kiln-dried lumber is not permitted. The lumber shall be certified C grade (standard) or better Douglas fir by a lumber grader at the mill of origin as specified in the West Coast Lumber Inspection Bureau Standard No. 16 (incorporated by reference—see §60.17).

7.1.2 Fuel Moisture. The test fuel shall have a moisture content range between 16 to 20 percent on a wet basis (19 to 25 percent dry basis). Addition of moisture to previously dried wood is not allowed. It is recommended that the test fuel be stored in a temperature and humidity-controlled room.

7.1.3 Fuel Temperature. The test fuel shall be at the test facility temperature of 18 to 32 °C (65 to 90 °F).

7.1.4 Fuel Dimensions. The dimensions of each test fuel piece shall conform to the nominal measurements of 2 × 4 and 4 × 4 lumber. Each piece of test fuel (not including spacers) shall be of equal length, except as necessary to meet requirements in section 8.8, and shall closely approximate 5⁄6 the dimensions of the length of the usable firebox. The fuel piece dimensions shall be determined in relation to the appliance's firebox volume according to guidelines listed below:

7.1.4.1 If the usable firebox volume is less than or equal to 0.043 m^3 (1.5 ft^3), use 2 × 4 lumber.

7.1.4.2 If the usable firebox volume is greater than 0.043 m^3 (1.5 ft^3) and less than or equal to 0.085 m^3 (3.0 ft^3), use 2 × 4 and 4 × 4 lumber. About half the weight of the test fuel charge shall be 2 × 4 lumber, and the remainder shall be 4 × 4 lumber.

7.1.4.3 If the usable firebox volume is greater than 0.085 m^3 (3.0 ft^3), use 4 × 4 lumber.

7.2 Test Fuel Spacers. Air-dried, Douglas fir lumber meeting the requirements outlined in sections 7.1.1 through 7.1.3. The spacers shall be 130 × 40 × 20 mm (5 × 1.5 × 0.75 in.).

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Test Run Requirements.

8.1.1 Burn Rate Categories. One emission test run is required in each of the following burn rate categories:

BURN RATE CATEGORIES

[Average kg/hr (lb/hr), dry basis]

Category 1	Category 2	Category 3	Category 4
<0.80 (<1.76)	0.80 to 1.25 (1.76 to 2.76)	1.25 to 1.90 (2.76 to 4.19)	Maximum. burn rate.

8.1.1.1 Maximum Burn Rate. For Category 4, the wood heater shall be operated with the primary air supply inlet controls fully open (or, if thermostatically controlled, the thermostat shall be set at maximum heat output) during the entire test run, or the maximum burn rate setting specified by the manufacturer's written instructions.

8.1.1.2 Other Burn Rate Categories. For burn rates in Categories 1 through 3, the wood heater shall be operated with the primary air supply inlet control, or other mechanical control device, set at a predetermined position necessary to obtain the average burn rate required for the category.

8.1.1.3 Alternative Burn Rates for Burn Rate Categories 1 and 2.

8.1.1.3.1 If a wood heater cannot be operated at a burn rate below 0.80 kg/hr (1.76 lb/hr), two test runs shall be conducted with burn rates within Category 2. If a wood heater cannot be operated at a burn rate below 1.25 kg/hr (2.76 lb/hr), the flue shall be dampered or the air supply otherwise controlled in order to achieve two test runs within Category 2.

8.1.1.3.2 Evidence that a wood heater cannot be operated at a burn rate less than 0.80 kg/hr shall include documentation of two or more attempts to operate the wood heater in burn rate Category 1 and fuel combustion has stopped, or results of two or more test runs demonstrating that the burn rates were greater than 0.80 kg/hr when the air supply controls were adjusted to the lowest possible position or settings. Stopped fuel combustion is evidenced when an elapsed time of 30 minutes or more has occurred without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change in the test fuel charge. See also section 8.8.3. Report the evidence and the reasoning used to determine that a test in burn rate Category 1 cannot be achieved; for example, two unsuccessful attempts to operate at a burn rate of 0.4 kg/hr are not sufficient evidence that burn rate Category 1 cannot be achieved.

NOTE: After July 1, 1990, if a wood heater cannot be operated at a burn rate less than 0.80 kg/hr, at least one test run with an average burn rate of 1.00 kg/hr or less shall be conducted. Additionally, if flue dampering must be used to achieve burn rates below 1.25

kg/hr (or 1.0 kg/hr), results from a test run conducted at burn rates below 0.90 kg/hr need not be reported or included in the test run average provided that such results are replaced with results from a test run meeting the criteria above.

8.2 Catalytic Combustor and Wood Heater Aging. The catalyst-equipped wood heater or a wood heater of any type shall be aged before the certification test begins. The aging procedure shall be conducted and documented by a testing laboratory accredited according to procedures in §60.535 of 40 CFR part 60.

8.2.1 Catalyst-equipped Wood Heater. Operate the catalyst-equipped wood heater using fuel meeting the specifications outlined in sections 7.1.1 through 7.1.3, or cordwood with a moisture content between 15 and 25 percent on a wet basis. Operate the wood heater at a medium burn rate (Category 2 or 3) with a new catalytic combustor in place and in operation for at least 50 hours. Record and report hourly catalyst exit temperature data (Section 8.6.2) and the hours of operation.

8.2.2 Non-Catalyst Wood Heater. Operate the wood heater using the fuel described in section 8.4.1 at a medium burn rate for at least 10 hours. Record and report the hours of operation.

8.3 Pretest Recordkeeping. Record the test fuel charge dimensions and weights, and wood heater and catalyst descriptions as shown in the example in Figure 28–1.

8.4 Wood Heater Installation. Assemble the wood heater appliance and parts in conformance with the manufacturer's written installation instructions. Place the wood heater centrally on the platform scale and connect the wood heater to the flue described in section 6.11. Clean the flue with an appropriately sized, wire chimney brush before each certification test.

8.5 Wood Heater Temperature Monitors.

8.5.1 For catalyst-equipped wood heaters, locate a temperature monitor (optional) about 25 mm (1 in.) upstream of the catalyst at the centroid of the catalyst face area, and locate a temperature monitor (mandatory) that will indicate the catalyst exhaust temperature. This temperature monitor is centrally located within 25 mm (1 in.) downstream at the centroid of catalyst face area. Record these locations.

8.5.2 Locate wood heater surface temperature monitors at five locations on the wood heater firebox exterior surface. Position the temperature monitors centrally on the top surface, on two sidewall surfaces, and on the bottom and back surfaces. Position the monitor sensing tip on the firebox exterior surface inside of any heat shield, air circulation walls, or other wall or shield separated from the firebox exterior surface. Surface temperature locations for unusual design shapes (*e.g.*, spherical, etc.) shall be positioned so that there are four surface temperature monitors in both the vertical and horizontal planes passing at right angles through the centroid of the firebox, not including the fuel loading door (total of five temperature monitors).

8.6 Test Facility Conditions.

8.6.1 Locate the test facility temperature monitor on the horizontal plane that includes the primary air intake opening for the wood heater. Locate the temperature monitor 1 to 2 m (3 to 6 ft) from the front of the wood heater in the 90° sector in front of the wood heater.

8.6.2 Use an anemometer to measure the air velocity. Measure and record the room air velocity before the pretest ignition period (Section 8.7) and once immediately following the test run completion.

8.6.3 Measure and record the test facility's ambient relative humidity, barometric pressure, and temperature before and after each test run.

8.6.4 Measure and record the flue draft or static pressure in the flue at a location no greater than 0.3 m (1 ft) above the flue connector at the wood heater exhaust during the test run at the recording intervals (Section 8.8.2).

8.7 Wood Heater Firebox Volume.

8.7.1 Determine the firebox volume using the definitions for height, width, and length in section 3. Volume adjustments due to presence of firebrick and other permanent fixtures may be necessary. Adjust width and length dimensions to extend to the metal wall of the wood heater above the firebrick or permanent obstruction if the firebrick or obstruction extending the length of the side(s) or back wall extends less than one-third of the usable firebox height. Use the width or length dimensions inside the firebrick if the firebrick extends more than one-third of the usable firebox height. If a log retainer or grate is a permanent fixture and the manufacturer recommends that no fuel be placed outside the retainer, the area outside of the retainer is excluded from the firebox volume calculations.

8.7.2 In general, exclude the area above the ash lip if that area is less than 10 percent of the usable firebox volume. Otherwise, take into account consumer loading practices. For instance, if fuel is to be loaded front-to-back, an ash lip may be considered usable firebox volume.

8.7.3 Include areas adjacent to and above a baffle (up to two inches above the fuel loading opening) if four inches or more horizontal space exist between the edge of the baffle and a vertical obstruction (*e.g.*, sidewalls or air channels).

8.8 Test Fuel Charge.

8.8.1 Prepare the test fuel pieces in accordance with the specifications outlined in sections 7.1 and 7.2. Determine the test fuel moisture content with a calibrated electrical resistance meter or other equivalent performance meter. If necessary, convert fuel moisture content values from dry basis (%M_d) to wet basis (%M_w) in section 12.2 using Equation 28–1. Determine fuel moisture for each fuel piece (not including spacers) by averaging at least three moisture meter readings, one from each of three sides, measured parallel to the wood grain. Average all the readings for all the fuel pieces in the test fuel charge. If an electrical resistance type meter is used, penetration of insulated electrodes shall be one-fourth the thickness of the test fuel piece or 19 mm (0.75 in.), whichever is greater. Measure the moisture content within a 4-hour period prior to the test run. Determine the fuel temperature by measuring the temperature of the room where the wood has been stored for at least 24 hours prior to the moisture determination.

8.8.2 Attach the spacers to the test fuel pieces with uncoated, ungalvanized nails or staples as illustrated in Figure 28–2. Attachment of spacers to the top of the test fuel piece(s) on top of the test fuel charge is optional.

8.8.3 To avoid stacking difficulties, or when a whole number of test fuel pieces does not result, all piece lengths shall be adjusted uniformly to remain within the specified loading density. The shape of the test fuel crib shall be geometrically similar to the shape of the firebox volume without resorting to special angular or round cuts on the individual fuel pieces.

8.8.4 The test fuel loading density shall be 112 ±11.2 kg/m^3 (7 ±0.7 lb/ft^3) of usable firebox volume on a wet basis.

8.9 Sampling Equipment. Prepare the sampling equipment as defined by the selected method (*i.e.*, either Method 5G or Method 5H). Collect one particulate emission sample for each test run.

8.10 Secondary Air Adjustment Validation.

8.10.1 If design drawings do not show the introduction of secondary air into a chamber outside the firebox (see ‘‘secondary air supply’’ under section 3.0, Definitions), conduct a separate test of the wood heater's secondary air supply. Operate the wood heater at a burn rate in Category 1 (Section 8.1.1) with the secondary air supply operated following the manufacturer's written instructions. Start the secondary air validation test run as described in section 8.8.1, except no emission sampling is necessary and burn rate data shall be recorded at 5-minute intervals.

8.10.2 After the start of the test run, operate the wood heater with the secondary air supply set as per the manufacturer's instructions, but with no adjustments to this setting. After 25 percent of the test fuel has been consumed, adjust the secondary air supply controls to another setting, as per the manufacturer's instructions. Record the burn rate data (5-minute intervals) for 20 minutes following the air supply adjustment.

8.10.3 Adjust the air supply control(s) to the original position(s), operate at this condition for at least 20 minutes, and repeat the air supply adjustment procedure above. Repeat the procedure three times at equal intervals over the entire burn period as defined in section 8.8. If the secondary air adjustment results in a burn rate change of more than an average of 25 percent between the 20-minute periods before and after the secondary adjustments, the secondary air supply shall be considered a primary air supply, and no adjustment to this air supply is allowed during the test run.

8.10.4 The example sequence below describes a typical secondary air adjustment validation check. The first cycle begins after at least 25 percent of the test fuel charge has been consumed.

Cycle 1
  Part 1, sec air adjusted to final position—20 min
  Part 2, sec air adjusted to final position—20 min
  Part 3, sec air adjusted to final position—20 min
Cycle 2
  Part 1, sec air adjusted to final position—20 min
  Part 2, sec air adjusted to final position—20 min
  Part 3, sec air adjusted to final position—20 min
Cycle 3
  Part 1, sec air adjusted to final position—20 min
  Part 2, sec air adjusted to final position—20 min
  Part 3, sec air adjusted to final position—20 min

Note that the cycles may overlap; that is, Part 3 of Cycle 1 may coincide in part or in total with Part 1 of Cycle 2. The calculation of the secondary air percent effect for this example is as follows:

$$\%BR_{sec} = \frac{\left|\overline{BR_{1,3}} - \overline{BR_2}\right|}{\overline{BR_{1,3}}} \times 100 \qquad \text{Eq. 28-1}$$

8.11 Pretest Ignition. Build a fire in the wood heater in accordance with the manufacturer's written instructions.

8.11.1 Pretest Fuel Charge. Crumpled newspaper loaded with kindling may be used to help ignite the pretest fuel. The pretest fuel, used to sustain the fire, shall meet the same fuel requirements prescribed in section 7.1. The pretest fuel charge shall consist of whole 2 × 4's that are no less than ⅓ the length of the test fuel pieces. Pieces of 4 × 4 lumber in approximately the same weight ratio as for the test fuel charge may be added to the pretest fuel charge.

8.11.2 Wood Heater Operation and Adjustments. Set the air inlet supply controls at any position that will maintain combustion of the pretest fuel load. At least one hour before the start of the test run, set the air supply controls at the approximate positions necessary to achieve the burn rate desired for the test run. Adjustment of the air supply controls, fuel addition or subtractions, and coalbed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coalbed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of uniform charcoalization. Record all adjustments made to the air supply controls, adjustments to and additions or subtractions of fuel, and any other changes to wood heater operations that occur during pretest ignition period. Record fuel weight data and wood heater temperature measurements at 10-minute intervals during the hour of the pretest ignition period preceding the start of the test run. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coalbed raking is the only adjustment allowed during this period.

NOTE: One purpose of the pretest ignition period is to achieve uniform charcoalization of the test fuel bed prior to loading the test fuel charge. Uniform charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run should be done to achieve uniform charcoalization while maintaining the desired burn rate. In addition, some wood heaters (*e.g.*, high mass units) may require extended pretest burn time and fuel additions to reach an initial average surface temperature sufficient to meet the thermal equilibrium criteria in section 8.3.

8.11.3 The weight of pretest fuel remaining at the start of the test run is determined as the difference between the weight of the wood heater with the remaining pretest fuel and the tare weight of the cleaned, dry wood heater with or without dry ash or sand added consistent with the manufacturer's instructions and the owner's manual. The tare weight of the wood heater must be determined with the wood heater (and ash, if added) in a dry condition.

8.12 Test Run. Complete a test run in each burn rate category, as follows:

8.12.1 Test Run Start.

8.12.1.1 When the kindling and pretest fuel have been consumed to leave a fuel weight between 20 and 25 percent of the weight of the test fuel charge, record the weight of the fuel remaining and start the test run. Record and report any other criteria, in addition to those specified in this section, used to determine the moment of the test run start (*e.g.*, firebox or catalyst temperature), whether such criteria are specified by the wood heater manufacturer or the testing laboratory. Record all wood heater individual surface temperatures, catalyst temperatures, any initial sampling method measurement values, and begin the particulate emission sampling. Within 1 minute following the start of the test run, open the wood heater door, load the test fuel charge, and record the test fuel charge weight. Recording of average, rather than individual, surface temperatures is acceptable for tests conducted in accordance with §60.533(o)(3)(i) of 40 CFR part 60.

8.12.1.2 Position the fuel charge so that the spacers are parallel to the floor of the firebox, with the spacer edges abutting each other. If loading difficulties result, some fuel pieces may be placed on edge. If the usable firebox volume is between 0.043 and 0.085 m^3 (1.5 and 3.0 ft^3), alternate the piece sizes in vertical stacking layers to the extent possible. For example, place 2 × 4's on the bottom layer in direct contact with the coal bed and 4 × 4's on the next layer, etc. (See Figure 28–3). Position the fuel pieces parallel to each other and parallel to the longest wall of the firebox to the extent possible within the specifications in section 8.8.

8.12.1.3 Load the test fuel in appliances having unusual or unconventional firebox design maintaining air space intervals between the test fuel pieces and in conformance with the manufacturer's written instructions. For any appliance that will not accommodate the loading arrangement specified in the paragraph above, the test facility personnel shall contact the Administrator for an alternative loading arrangement.

8.12.1.4 The wood heater door may remain open and the air supply controls adjusted up to five minutes after the start of the test run in order to make adjustments to the test fuel charge and to ensure ignition of the test fuel charge has occurred. Within the five minutes after the start of the test run, close the wood heater door and adjust the air supply controls to the position determined to produce the desired burn rate. No other adjustments to the air supply controls or the test fuel charge are allowed (except as specified in sections 8.12.3 and 8.12.4) after the first five minutes of the test run. Record the length of time the wood heater door remains open, the adjustments to the air supply controls, and any other operational adjustments.

8.12.2 Data Recording. Record on a data sheet similar to that shown in Figure 28–4, at intervals no greater than 10 minutes, fuel weight data, wood heater individual surface and catalyst temperature measurements, other wood heater operational data (*e.g.*, draft), test facility temperature and sampling method data.

8.12.3 Test Fuel Charge Adjustment. The test fuel charge may be adjusted (*i.e.*, repositioned) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (<0.05 kg (0.1 lb) or 1.0 percent, whichever is greater) weight change. The time used to make this adjustment shall be less than 15 seconds.

8.12.4 Air Supply Adjustment. Secondary air supply controls may be adjusted once during the test run following the manufacturer's written instructions (see section 8.10). No other air supply adjustments are allowed during the test run. Recording of wood heater flue draft during the test run is optional for tests conducted in accordance with § 60.533(o)(3)(i) of 40 CFR part 60.

8.12.5 Auxiliary Wood Heater Equipment Operation. Heat exchange blowers sold with the wood heater shall be operated during the test run following the manufacturer's written instructions. If no manufacturer's written instructions are available, operate the heat exchange blower in the ''high'' position. (Automatically operated blowers shall be operated as designed.) Shaker grates, by-pass controls, or other auxiliary equipment may be adjusted only one time during the test run following the manufacturer's written instructions.

Record all adjustments on a wood heater operational written record.

NOTE: If the wood heater is sold with a heat exchange blower as an option, test the wood heater with the heat exchange blower operating as described in sections 8.1 through 8.12 and report the results. As an alternative to repeating all test runs without the heat exchange blower operating, one additional test run may be without the blower operating as described in section 8.12.5 at a burn rate in Category 2 (Section 8.1.1). If the emission rate resulting from this test run without the blower operating is equal to or less than the emission rate plus 1.0 g/hr (0.0022 lb/hr) for the test run in burn rate Category 2 with the blower operating, the wood heater may be considered to have the same average emission rate with or without the blower operating. Additional test runs without the blower operating are unnecessary.

8.13 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. The test run is completed when the remaining weight of the test fuel charge is 0.00 kg (0.0 lb). End the test run when the scale has indicated a test fuel charge weight of 0.00 kg (0.0 lb) or less for 30 seconds. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values.

8.14 Wood Heater Thermal Equilibrium. The average of the wood heater surface temperatures at the end of the test run shall agree with the average surface temperature at the start of the test run to within 70 °C (126 °F).

8.15 Consecutive Test Runs. Test runs on a wood heater may be conducted consecutively provided that a minimum one-hour interval occurs between test runs.

8.16 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the burn rate categories specified in section 8.1.1. If more than one test run is conducted at a specified burn rate, the results from at least two-thirds of the test runs in that burn rate category shall be used in calculating the weighted average emission rate (see section 12.2). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate (see note in section 8.1).

9.0 Quality Control

Same as section 9.0 of either Method 5G or Method 5H.

10.0 Calibration and Standardizations

Same as section 10.0 of either Method 5G or Method 5H, with the addition of the following:

10.1 Platform Scale. Perform a multi-point calibration (at least five points spanning the operational range) of the platform scale before its initial use. The scale manufacturer's calibration results are sufficient for this purpose. Before each certification test, audit the scale with the wood heater in place by weighing at least one calibration weight (Class F) that corresponds to between 20 percent and 80 percent of the expected test fuel charge weight. If the scale cannot reproduce the value of the calibration weight within 0.05 kg (0.1 lb) or 1 percent of the expected test fuel charge weight, whichever is greater, recalibrate the scale before use with at least five calibration weights spanning the operational range of the scale.

10.2 Balance (optional). Calibrate as described in section 10.1.

10.3 Temperature Monitor. Calibrate as in Method 2, section 4.3, before the first certification test and semiannually thereafter.

10.4 Moisture Meter. Calibrate as per the manufacturer's instructions before each certification test.

10.5 Anemometer. Calibrate the anemometer as specified by the manufacturer's instructions before the first certification test and semiannually thereafter.

10.6 Barometer. Calibrate against a mercury barometer before the first certification test and semiannually thereafter.

10.7 Draft Gauge. Calibrate as per the manufacturer's instructions; a liquid manometer does not require calibration.

10.8 Humidity Gauge. Calibrate as per the manufacturer's instructions before the first certification test and semiannually thereafter.

11.0 Analytical Procedures

Same as section 11.0 of either Method 5G or Method 5H.

12.0 Data Analysis and Calculations

Same as section 12.0 of either Method 5G or Method 5H, with the addition of the following:

12.1 Nomenclature.

BR = Dry wood burn rate, kg/hr (lb/hr)
E_i = Emission rate for test run, i, from Method 5G or 5H, g/hr (lb/hr)
E_w = Weighted average emission rate, g/hr (lb/hr)
k_i = Test run weighting factor = $P_{i+1} - P_{i-1}$
$\%M_d$ = Fuel moisture content, dry basis, percent.
$\%M_w$ = Average moisture in test fuel charge, wet basis, percent.
n = Total number of test runs.
P_i = Probability for burn rate during test run, i, obtained from Table 28–1. Use linear interpolation to determine probability values for burn rates between those listed on the table.
W_{wd} = Total mass of wood burned during the test run, kg (lb).

12.2 Wet Basis Fuel Moisture Content.

$$\%M_w = \frac{100(\%M_d)}{100 + \%M_d} \qquad \text{Eq. 28-2}$$

12.3 Weighted Average Emission Rate. Calculate the weighted average emission rate (E_w) using Equation 28–1:

$$E_w = \frac{\sum_{i=1}^{n}(K_i E_i)}{\sum_{i=1}^{n} K_i} \qquad \text{Eq. 28-3}$$

NOTE: P_o always equals 0, $P_{(n+1)}$ always equals 1, P_1 corresponds to the probability of the lowest recorded burn rate, P_2 corresponds to the probability of the next lowest burn rate, etc. An example calculation is in section 12.3.1.

12.3.1 Example Calculation of Weighted Average Emission Rate.

Burn rate category	Test No.	Burn rate (Dry-kg/hr)	Emissions (g/hr)
1	1	0.65	5.0
2[1]	2	0.85	6.7
2	3	0.90	4.7
2	4	1.00	5.3
3	5	1.45	3.8
4	6	2.00	5.1

[1] As permitted in section 6.6, this test run may be omitted from the calculation of the weighted average emission rate because three runs were conducted for this burn rate category.

Test No.	Burn rate	P_i	E_i	K_i
0		0.000		
1	0.65	0.121	5.0	0.300
2	0.90	0.300	4.7	0.259
3	1.00	0.380	5.3	0.422
4	1.45	0.722	3.8	0.532
5	2.00	0.912	5.1	0.278
6		1.000		

$K_1 = P_2 - P_0 = 0.300 - 0 = 0.300$
$K_2 = P_3 - P_1 = 0.381 - 0.121 = 0.259$
$K_3 = P_4 - P_2 = 0.722 - 0.300 = 0.422$
$K_4 = P_5 - P_3 = 0.912 - 0.380 = 0.532$
$K_5 = P_6 - P_4 = 1.000 - 0.722 = 0.278$

Weighted Average Emission Rate, E_w, Calculation

$$
\begin{aligned}
E_w &= \frac{\sum (K_i E_i)}{\sum K_i} \\
&= \frac{(0.3)(5.0)+(0.259)(4.7)+(0.422)(5.3)+(0.532)(3.8)+(0.278)(5.1)}{1.791} \\
&= 4.69\ \mathrm{g/hr}
\end{aligned}
$$

12.4 Average Wood Heater Surface Temperatures. Calculate the average of the wood heater surface temperatures for the start of the test run (Section 8.12.1) and for the test run completion (Section 8.13). If the two average temperatures do not agree within 70 °C (125 °F), report the test run results, but do not include the test run results in the test average. Replace such test run results with results from another test run in the same burn rate category.

12.5 Burn Rate. Calculate the burn rate (BR) using Equation 28–3:

$$BR = \frac{60 W_{wd}}{\theta} \times \frac{100 - \%M_w}{100} \qquad \text{Eq. 28-3}$$

12.6 Reporting Criteria. Submit both raw and reduced test data for wood heater tests.

12.6.1 Suggested Test Report Format.

12.6.1.1 Introduction.

12.6.1.1.1 Purpose of test-certification, audit, efficiency, research and development.

12.6.1.1.2 Wood heater identification-manufacturer, model number, catalytic/noncatalytic, options.

12.6.1.1.3 Laboratory-name, location (altitude), participants.

12.6.1.1.4 Test information-date wood heater received, date of tests, sampling methods used, number of test runs.

12.6.1.2 Summary and Discussion of Results

12.6.1.2.1 Table of results (in order of increasing burn rate)-test run number, burn rate, particulate emission rate, efficiency (if determined), averages (indicate which test runs are used).

12.6.1.2.2 Summary of other data-test facility conditions, surface temperature averages, catalyst temperature averages, pretest fuel weights, test fuel charge weights, run times.

12.6.1.2.3 Discussion-Burn rate categories achieved, test run result selection, specific test run problems and solutions.

12.6.1.3 Process Description.

12.6.1.3.1 Wood heater dimensions-volume, height, width, lengths (or other linear dimensions), weight, volume adjustments.

12.6.1.3.2 Firebox configuration-air supply locations and operation, air supply introduction location, refractory location and dimensions, catalyst location, baffle and by-pass location and operation (include line drawings or photographs).

12.6.1.3.3 Process operation during test-air supply settings and adjustments, fuel bed adjustments, draft.

12.6.1.3.4 Test fuel-test fuel properties (moisture and temperature), test fuel crib description (include line drawing or photograph), test fuel loading density.

12.6.1.4 Sampling Locations.

12.6.1.4.1 Describe sampling location relative to wood heater. Include drawing or photograph.

12.6.1.5 Sampling and Analytical Procedures

12.6.1.5.1 Sampling methods-brief reference to operational and sampling procedures and optional and alternative procedures used.

12.6.1.5.2 Analytical methods-brief description of sample recovery and analysis procedures.

12.6.1.6 Quality Control and Assurance Procedures and Results

12.6.1.6.1 Calibration procedures and results-certification procedures, sampling and analysis procedures.

12.6.1.6.2 Test method quality control procedures-leak-checks, volume meter checks, stratification (velocity) checks, proportionality results.

12.6.1.7 Appendices

12.6.1.7.1 Results and Example Calculations. Complete summary tables and accompanying examples of all calculations.

12.6.1.7.2 Raw Data. Copies of all uncorrected data sheets for sampling measurements, temperature records and sample recovery data. Copies of all pretest burn rate and wood heater temperature data.

12.6.1.7.3 Sampling and Analytical Procedures. Detailed description of procedures followed by laboratory personnel in conducting the certification test, emphasizing particular parts of the procedures differing from the methods (*e.g.*, approved alternatives).

12.6.1.7.4 Calibration Results. Summary of all calibrations, checks, and audits pertinent to certification test results with dates.

12.6.1.7.5 Participants. Test personnel, manufacturer representatives, and regulatory observers.

12.6.1.7.6 Sampling and Operation Records. Copies of uncorrected records of activities not included on raw data sheets (*e.g.*, wood heater door open times and durations).

12.6.1.7.7 Additional Information. Wood heater manufacturer's written instructions for operation during the certification test.

12.6.2.1 Wood Heater Identification. Report wood heater identification information. An example data form is shown in Figure 28–4.

12.6.2.2 Test Facility Information. Report test facility temperature, air velocity, and humidity information. An example data form is shown on Figure 28–4.

12.6.2.3 Test Equipment Calibration and Audit Information. Report calibration and audit results for the platform scale, test fuel balance, test fuel moisture meter, and sampling equipment including volume metering systems and gaseous analyzers.

12.6.2.4 Pretest Procedure Description. Report all pretest procedures including pretest fuel weight, burn rates, wood heater temperatures, and air supply settings. An example data form is shown on Figure 28–4.

12.6.2.5 Particulate Emission Data. Report a summary of test results for all test runs and the weighted average emission rate. Submit copies of all data sheets and other records collected during the testing. Submit examples of all calculations.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Pellet Burning Heaters. Certification testing requirements and procedures for pellet burning wood heaters are identical to those for other wood heaters, with the following exceptions:

16.1.1 Test Fuel Properties. The test fuel shall be all wood pellets with a moisture content no greater than 20 percent on a wet basis (25 percent on a dry basis). Determine the wood moisture content with either ASTM D 2016–74 or 83, (Method A), ASTM D 4444–92, or ASTM D 4442–84 or 92 (all noted ASTM standards are incorporated by reference—see §60.17).

16.1.2 Test Fuel Charge Specifications. The test fuel charge size shall be as per the manufacturer's written instructions for maintaining the desired burn rate.

16.1.3 Wood Heater Firebox Volume. The firebox volume need not be measured or determined for establishing the test fuel charge size. The firebox dimensions and other heater specifications needed to identify the heater for certification purposes shall be reported.

16.1.4 Heater Installation. Arrange the heater with the fuel supply hopper on the platform scale as described in section 8.6.1.

16.1.5 Pretest Ignition. Start a fire in the heater as directed by the manufacturer's written instructions, and adjust the heater controls to achieve the desired burn rate. Operate the heater at the desired burn rate for at least 1 hour before the start of the test run.

16.1.6 Test Run. Complete a test run in each burn rate category as follows:

16.1.6.1 Test Run Start. When the wood heater has operated for at least 1 hour at the desired burn rate, add fuel to the supply hopper as necessary to complete the test run, record the weight of the fuel in the supply hopper (the wood heater weight), and start the test run. Add no additional fuel to the hopper during the test run.

Record all the wood heater surface temperatures, the initial sampling method measurement values, the time at the start of the test, and begin the emission sampling. Make no adjustments to the wood heater air supply or wood supply rate during the test run.

16.1.6.2 Data Recording. Record the fuel (wood heater) weight data, wood heater temperature and operational data, and emission sampling data as described in section 8.12.2.

16.1.6.3 Test Run Completion. Continue emission sampling and wood heater operation for 2 hours. At the end of the test run, stop the particulate sampling, and record the final fuel weight, the run time, and all final measurement values, including all wood heater individual surface temperatures.

16.1.7 Calculations. Determine the burn rate using the difference between the initial and final fuel (wood heater) weights and the procedures described in section 12.4. Complete the other calculations as described in section 12.0.

17.0 References

Same as Method 5G, with the addition of the following:

1. Radian Corporation. OMNI Environmental Services, Inc., Cumulative Probability for a Given Burn Rate Based on Data Generated in the CONEG and BPA Studies. Package of materials submitted to the Fifth Session of the Regulatory Negotiation Committee, July 16–17, 1986.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 28–1—BURN RATE WEIGHTED PROBABILITIES FOR CALCULATING WEIGHTED AVERAGE EMISSION RATES

Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)	Burn rate (kg/hr-dry)	Cumulative probability (P)
0.00	0.000	1.70	0.840	3.40	0.989
0.05	0.002	1.75	0.857	3.45	0.989
0.10	0.007	1.80	0.875	3.50	0.990
0.15	0.012	1.85	0.882	3.55	0.991
0.20	0.016	1.90	0.895	3.60	0.991
0.25	0.021	1.95	0.906	3.65	0.992
0.30	0.028	2.00	0.912	3.70	0.992
0.35	0.033	2.05	0.920	3.75	0.992
0.40	0.041	2.10	0.925	3.80	0.993
0.45	0.054	2.15	0.932	3.85	0.994
0.50	0.065	2.20	0.936	3.90	0.994
0.55	0.086	2.25	0.940	3.95	0.994
0.60	0.100	2.30	0.945	4.00	0.994
0.65	0.121	2.35	0.951	4.05	0.995
0.70	0.150	2.40	0.956	4.10	0.995
0.75	0.185	2.45	0.959	4.15	0.995
0.80	0.220	2.50	0.964	4.20	0.995
0.85	0.254	2.55	0.968	4.25	0.995
0.90	0.300	2.60	0.972	4.30	0.996
0.95	0.328	2.65	0.975	4.35	0.996
1.00	0.380	2.70	0.977	4.40	0.996
1.05	0.407	2.75	0.979	4.45	0.996
1.10	0.460	2.80	0.980	4.50	0.996
1.15	0.490	2.85	0.981	4.55	0.996
1.20	0.550	2.90	0.982	4.60	0.996
1.25	0.572	2.95	0.984	4.65	0.996
1.30	0.620	3.00	0.984	4.70	0.996
1.35	0.654	3.05	0.985	4.75	0.997
1.40	0.695	3.10	0.986	4.80	0.997
1.45	0.722	3.15	0.987	4.85	0.997
1.50	0.750	3.20	0.987	4.90	0.997
1.55	0.779	3.25	0.988	4.95	0.997
1.60	0.800	3.30	0.988	≥5.00	1.000
1.65	0.825	3.35	0.989		

Appliance Identification

Appliance Manufacturer ________________________________ Address ____

________________________________ Agent and phone number ____

________________________________ Name and Model number ____________

________________________ Weight ________________________

______________ Serial number ____________________

Design: Catalytic __________ Noncatalytic __________

Insert __________ Freestanding __________

Woodheater Description: (Attach figure showing air supplies and firebox configuration)

Materials of construction: ________________________________

____

____

____

Air Introduction System: ________________________________

____

____

____

Combustion Control Mechanisms: ________________________________

____

____

____

Internal Baffles: ________________________________

____

____

____

Other Features: ________________________________

____

____

Catalyst Specifications

Manufacturer ________________

Serial Number ________________

Age ________________(Hours)

Dimensions ________________(in.)

Firebox Dimensions

Volume ________________(ft^3)

Length ________________(in.)

Width ________________(in.)

Height ________________(in.)

Adjustments (Describe) ______(in.)

Test Fuel Information

(for each Test Run)

Weight of Test Change ________(lb)

Number of 2 × 4's __________

Number of 4 × 4's __________

Length of test pieces ______(in.)

Fuel Grade (Certification) ________Fuel

Moisture Content ________(%)

Diagram or Photograph of Test Fuel Crib

Figure 28-1. Wood Heater and Test Fuel Information.

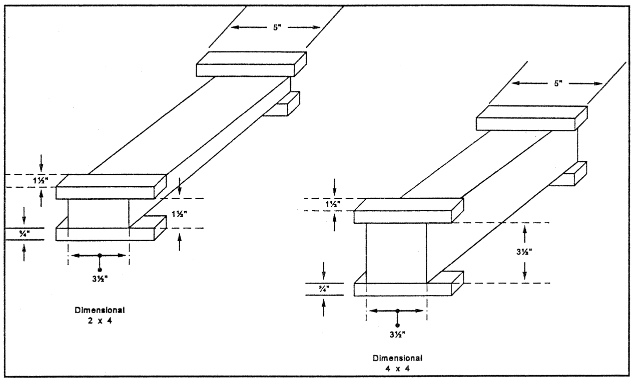


Figure 28-2. Test Fuel Spacer Dimensions.

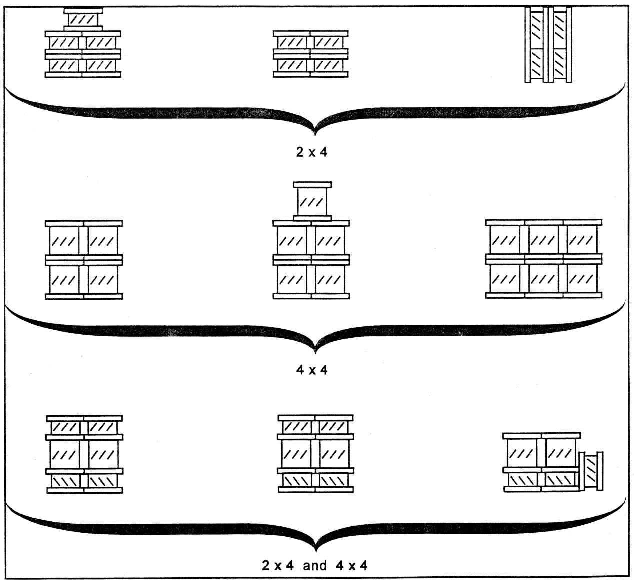
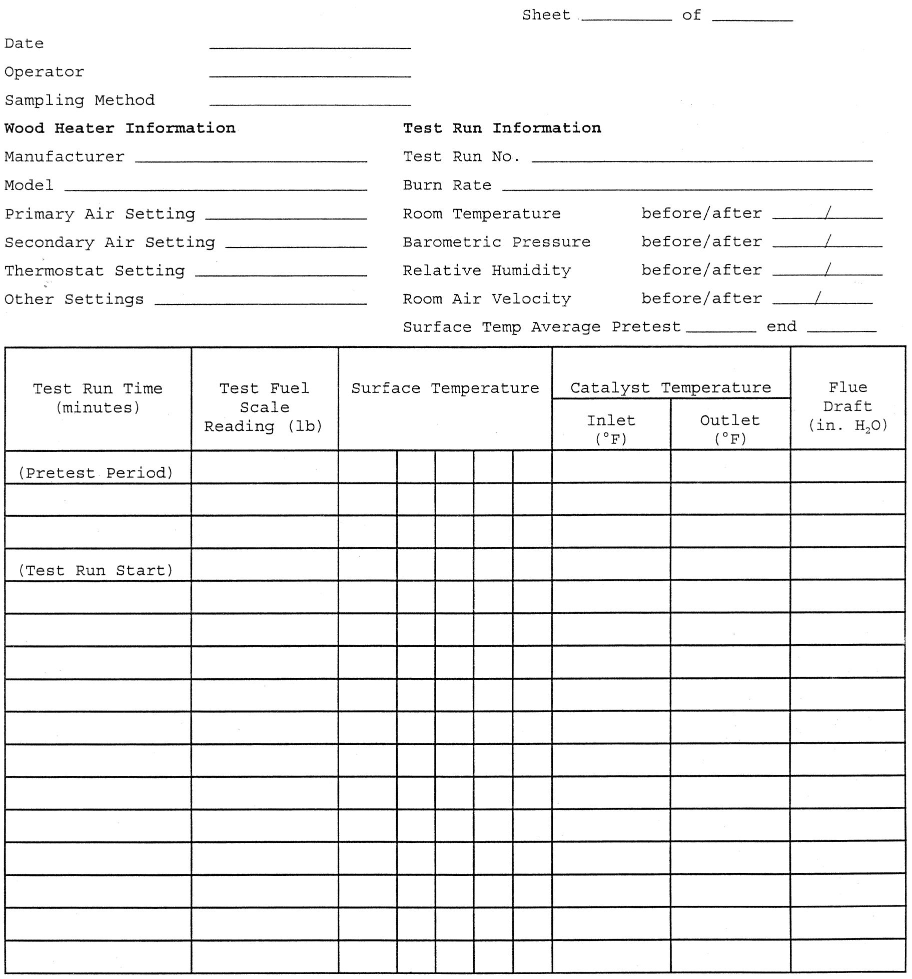


Figure 28-3. Test Fuel Crib Arrangements.



Sheet ________ of ________

Date ____________________

Operator ____________________

Sampling Method ____________________

Wood Heater Information

Manufacturer ____________________

Model ____________________

Primary Air Setting ____________________

Secondary Air Setting ____________________

Thermostat Setting ____________________

Other Settings ____________________

Test Run Information

Test Run No. ____________________

Burn Rate ____________________

Room Temperature before/after _____/_____

Barometric Pressure before/after _____/_____

Relative Humidity before/after _____/_____

Room Air Velocity before/after _____/_____

Surface Temp Average Pretest _______ end _______

Test Run Time (minutes)	Test Fuel Scale Reading (lb)	Surface Temperature					Catalyst Temperature		Flue Draft (in. H_2O)
							Inlet (°F)	Outlet (°F)	
(Pretest Period)									
(Test Run Start)									

Figure 28-4. Test Run Wood Heater Operation Data Sheet.

METHOD 28A—MEASUREMENT OF AIR- TO-FUEL RATIO AND MINIMUM ACHIEVABLE BURN RATES FOR WOOD-FIRED APPLIANCES

NOTE: This method does not include all or 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 at least the following additional test methods: Method 3, Method 3A, Method 5H, Method 6C, and Method 28.

1.0 Scope and Application

1.1 Analyte. Particulate matter (PM). No CAS number assigned.

1.2 Applicability. This method is applicable for the measurement of air-to-fuel ratios and minimum achievable burn rates, for determining whether a wood-fired appliance is an affected facility, as specified in 40 CFR 60.530.

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 a location in the stack of a wood-fired appliance while the appliance is operating at a prescribed set of conditions. The gas sample is analyzed for carbon dioxide (CO_2), oxygen (O_2), and carbon monoxide (CO). These stack gas components are measured for determining the dry molecular weight of the exhaust gas. Total moles of exhaust gas are determined stoichiometrically. Air-to-fuel ratio is determined by relating the mass of dry combustion air to the mass of dry fuel consumed.

3.0 Definitions

Same as Method 28, section 3.0, with the addition of the following:

3.1 Air-to-fuel ratio means the ratio of the mass of dry combustion air introduced into the firebox to the mass of dry fuel consumed (grams of dry air per gram of dry wood burned).

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

6.1 Test Facility. Insulated Solid Pack Chimney, Platform Scale and Monitor, Test Facility Temperature Monitor, Balance, Moisture Meter, Anemometer, Barometer, Draft Gauge, Humidity Gauge, Wood Heater Flue, and Test Facility. Same as Method 28, sections 6.1, 6.2, and 6.4 to 6.12, respectively.

6.2 Sampling System. Probe, Condenser, Valve, Pump, Rate Meter, Flexible Bag, Pressure Gauge, and Vacuum Gauge. Same as Method 3, sections 6.2.1 to 6.2.8, respectively. Alternatively, the sampling system described in Method 5H, section 6.1 may be used.

6.3 Exhaust Gas Analysis. Use one or both of the following:

6.3.1 Orsat Analyzer. Same as Method 3, section 6.1.3

6.3.2 Instrumental Analyzers. Same as Method 5H, sections 6.1.3.4 and 6.1.3.5, for CO_2 and CO analyzers, except use a CO analyzer with a range of 0 to 5 percent and use a CO_2 analyzer with a range of 0 to 5 percent. Use an O_2 analyzer capable of providing a measure of O_2 in the range of 0 to 25 percent by volume at least once every 10 minutes.

7.0 Reagents and Standards

7.1 Test Fuel and Test Fuel Spacers. Same as Method 28, sections 7.1 and 7.2, respectively.

7.2 Cylinder Gases. For each of the three analyzers, use the same concentration as specified in sections 7.2.1, 7.2.2, and 7.2.3 of Method 6C.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Wood Heater Air Supply Adjustments.

8.1.1 This section describes how dampers are to be set or adjusted and air inlet ports closed or sealed during Method 28A tests. The specifications in this section are intended to ensure that affected facility determinations are made on the facility configurations that could reasonably be expected to be employed by the user. They are also intended to prevent circumvention of the standard through the addition of an air port that would often be blocked off in actual use. These specifications are based on the assumption that consumers will remove such items as dampers or other closure mechanism stops if this can be done readily with household tools; that consumers will block air inlet passages not visible during normal operation of the appliance using aluminum tape or parts generally available at retail stores; and that consumers will cap off any threaded or flanged air inlets. They also assume that air leakage around glass doors, sheet metal joints or through inlet grilles visible during normal operation of the appliance would not be further blocked or taped off by a consumer.

8.1.2 It is not the intention of this section to cause an appliance that is clearly designed, intended, and, in most normal installations, used as a fireplace to be converted into a wood heater for purposes of applicability testing. Such a fireplace would be identifiable by such features as large or multiple glass doors or panels that are not gasketed, relatively unrestricted air inlets intended, in large part, to limit smoking and fogging of glass surfaces, and other aesthetic features not normally included in wood heaters.

8.1.3 Adjustable Air Supply Mechanisms. Any commercially available flue damper, other adjustment mechanism or other air inlet port that is designed, intended or otherwise reasonably expected to be adjusted or closed by consumers, installers, or dealers and which could restrict air into the firebox shall be set so as to achieve minimum air into the firebox (*i.e.*, closed off or set in the most closed position).

8.1.3.1 Flue dampers, mechanisms and air inlet ports which could reasonably be expected to be adjusted or closed would include:

8.1.3.1.1 All internal or externally adjustable mechanisms (including adjustments that affect the tightness of door fittings) that are accessible either before and/or after installation.

8.1.3.1.2 All mechanisms, other inlet ports, or inlet port stops that are identified in the owner's manual or in any dealer literature as being adjustable or alterable. For example, an inlet port that could be used to provide access to an outside air duct but which is identified as being closable through use of additional materials whether or not they are supplied with the facility.

8.1.3.1.3 Any combustion air inlet port or commercially available flue damper or mechanism stop, which would readily lend itself to closure by consumers who are handy with household tools by the removal of parts or the addition of parts generally available at retail stores (*e.g.*, addition of a pipe cap or plug, addition of a small metal plate to an inlet hole on a nondecorative sheet metal surface, or removal of riveted or screwed damper stops).

8.1.3.1.4 Any flue damper, other adjustment mechanisms or other air inlet ports that are found and documented in several (*e.g.*, a number sufficient to reasonably conclude that the practice is not unique or uncommon) actual installations as having been adjusted to a more closed position, or closed by consumers, installers, or dealers.

8.1.4 Air Supply Adjustments During Test. The test shall be performed with all air inlets identified under this section in the closed or most closed position or in the configuration which otherwise achieves the lowest air inlet (*i.e.*, greatest blockage).

NOTE: For the purposes of this section, air flow shall not be minimized beyond the point necessary to maintain combustion or beyond the point that forces smoke into the room.

8.1.5 Notwithstanding section 8.1.1, any flue damper, adjustment mechanism, or air inlet port (whether or not equipped with flue dampers or adjusting mechanisms) that is visible during normal operation of the appliance and which could not reasonably be closed further or blocked except through means that would significantly degrade the aesthetics of the facility (*e.g.*, through use of duct tape) will not be closed further or blocked.

8.2 Sampling System.

8.2.1 Sampling Location. Same as Method 5H, section 8.1.2.

8.2.2 Sampling System Set Up. Set up the sampling equipment as described in Method 3, section 8.1.

8.3 Wood Heater Installation, Test Facility Conditions, Wood Heater Firebox Volume, and Test Fuel Charge. Same as Method 28, sections 8.4 and 8.6 to 8.8, respectively.

8.4 Pretest Ignition. Same as Method 28, section 8.11. Set the wood heater air supply settings to achieve a burn rate in Category 1 or the lowest achievable burn rate (see section 8.1).

8.5 Test Run. Same as Method 28, section 8.12. Begin sample collection at the start of the test run as defined in Method 28, section 8.12.1.

8.5.1 Gas Analysis.

8.5.1.1 If Method 3 is used, collect a minimum of two bag samples simultaneously at a constant sampling rate for the duration of the test run. A minimum sample volume of 30 liters (1.1 ft^3) per bag is recommended.

8.5.1.2 If instrumental gas concentration measurement procedures are used, conduct the gas measurement system performance tests, analyzer calibration, and analyzer calibration error check outlined in Method 6C, sections 8.2.3, 8.2.4, 8.5, and 10.0, respectively. Sample at a constant rate for the duration of the test run.

8.5.2 Data Recording. Record wood heater operational data, test facility temperature, sample train flow rate, and fuel weight data at intervals of no greater than 10 minutes.

8.5.3 Test Run Completion. Same as Method 28, section 8.13.

9.0 Quality Control

9.1 Data Validation. The following quality control procedure is suggested to provide a check on the quality of the data.

9.1.1 Calculate a fuel factor, F_o, using Equation 28A–1 in section 12.2.

9.1.2 If CO is present in quantities measurable by this method, adjust the O_2 and CO_2 values before performing the calculation for F_o as shown in section 12.3 and 12.4.

9.1.3 Compare the calculated F_o factor with the expected F_o range for wood (1.000–1.120). Calculated F_o values beyond this acceptable range should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air. If no detectable or correctable measurement error can be identified, the test should be repeated. Alternatively, determine a range of air-to-fuel ratio results that could include the correct value by using an F_o value of 1.05 and calculating a potential range of CO_2 and O_2 values. Acceptance of such results will be based on whether the calculated range includes the exemption limit and the judgment of the Administrator.

9.2 Method 3 Analyses. Compare the results of the analyses of the two bag samples. If all the gas components (O_2, CO, and CO_2) values for the two analyses agree within 0.5 percent (*e.g.*, 6.0 percent O_2 for bag 1 and 6.5 percent O_2 for bag 2, agree within 0.5 percent), the results of the bag analyses may be averaged for the calculations in section 12. If the analysis results do not agree within 0.5 percent for each component, calculate the air-to-fuel ratio using both sets of analyses and report the results.

10.0 Calibration and Standardization

[Reserved]

11.0 Analytical Procedures

11.1 Method 3 Integrated Bag Samples. Within 4 hours after the sample collection, analyze each bag sample for percent CO_2, O_2, and CO using an Orsat analyzer as described in Method 3, section 11.0.

11.2 Instrumental Analyzers. Average the percent CO_2, CO, and O_2 values for the test run.

12.0 Data Analyses and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figure after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

N_T = Total gram-moles of dry exhaust gas per kg of wood burned (lb-moles/lb).

$\%CO_2$ = Percent CO_2 by volume (dry basis).

%CO = Percent CO by volume (dry basis).

$\%N_2$ = Percent N_2 by volume (dry basis).

$\%O_2$ = Percent O2 by volume (dry basis).

Y_{HC} = Assumed mole fraction of HC (dry as CH_4) = 0.0088 for catalytic wood heaters; = 0.0132 for noncatalytic wood heaters. = 0.0080 for pellet-fired wood heaters.

Y_{CO} = Measured mole fraction of CO (*e.g.*, 1 percent CO = .01 mole fraction), g/g-mole (lb/lb-mole).

Y_{CO2} = Measured mole fraction of CO_{CO2} (*e.g.*, 10 percent CO_2 = .10 mole fraction), g/g-mole (lb/lb-mole).

0.280 = Molecular weight of N_2 or CO, divided by 100.

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100.

20.9 = Percent O_2 by volume in ambient air.

42.5 = Gram-moles of carbon in 1 kg of dry wood assuming 51 percent carbon by weight dry basis (.0425 lb/lb-mole).

510 = Grams of carbon in exhaust gas per kg of wood burned.

1,000 = Grams in 1 kg.

12.2 Fuel Factor. Use Equation 28A–1 to calculate the fuel factor.

$$F_o = \frac{20.9 - \%O_2}{\%CO_2} \qquad \text{Eq. 28A-1}$$

12. 3 Adjusted $\%CO_2$. Use Equation 28A–2 to adjust CO_2 values if measurable CO is present.

$$\%CO_{2(adj)} = \%CO_2 + \%CO \qquad \text{Eq. 28A-2}$$

12.4 Adjusted $\%O_2$. Use Equation 28A–3 to adjust O_2 value if measurable CO is present.

$$\%O_{2(adj)} = \%O_2 - 0.5\%CO \qquad \text{Eq. 28A-3}$$

12.5 Dry Molecular Weight. Use Equation 28A–4 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO) \qquad \text{Eq. 28A-4}$$

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.9). A negative error of about 0.4 percent is introduced. Argon may be included in the analysis using procedures subject to approval of the Administrator.

12.6 Dry Moles of Exhaust Gas. Use Equation 28A–5 to calculate the total moles of dry exhaust gas produced per kilogram of dry wood burned.

$$N_T = \frac{42.5}{\left(Y_{CO_2} + Y_{CO} + Y_{HC}\right)} \qquad \text{Eq. 28A-5}$$

12.7 Air-to-Fuel Ratio. Use Equation 28A–6 to calculate the air-to-fuel ratio on a dry mass basis.

$$A/F = \frac{\left(N_T \times M_d\right) - 510}{1{,}000} \qquad \text{Eq. 28A-6}$$

12.8 Burn Rate. Calculate the fuel burn rate as in Method 28, section 12.4.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 16.0 of Method 3 and section 17 of Method 5G.

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

TEST METHOD 28R FOR CERTIFICATION AND AUDITING OF WOOD HEATERS

1.0 Scope and Application

1.1 This test method applies to certification and auditing of wood-fired room heaters and fireplace inserts.

1.2 The test method covers the fueling and operating protocol for measuring particulate emissions, as well as determining burn rates, heat output and efficiency.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

2.0 Procedures

2.1 This method incorporates the provisions of ASTM E2780–10 (IBR, see §60.17) except as follows:

2.1.1 The burn rate categories, low burn rate requirement, and weightings in Method 28 shall be used.

2.1.2 The startup procedures shall be the same as in Method 28.

2.1.3 Manufacturers shall not specify a smaller volume of the firebox for testing than the full usable firebox.

2.1.4 Prior to testing, the heater must be operated for a minimum of 50 hours using a medium burn rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement.

2.2 Manufacturers may use ASTM E871–82 (reapproved 2013) (IBR, see §60.17) as an alternative to the procedures in Method 5H or Method 28 for determining total weight basis moisture in the analysis sample of particulate wood fuel.

TEST METHOD 28WHH FOR MEASUREMENT OF PARTICULATE EMISSIONS AND HEATING EFFICIENCY OF WOOD-FIRED HYDRONIC HEATING APPLIANCES

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture.

1.2 The test method measures particulate emissions and delivered heating efficiency at specified heat output rates based on the appliance's rated heating capacity.

1.3 Particulate emissions are measured by the dilution tunnel method as specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used. Delivered efficiency is measured by determining the heat output through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and determining the input from the mass of dry wood fuel and its higher heating value. Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized heating appliances intended to be fired with wood. These products are wood-fired hydronic heating appliances that the manufacturer specifies for indoor or outdoor installation. They are often connected to a heat exchanger by insulated pipes and normally include a pump to circulate heated liquid. They are used to heat structures such as homes, barns and greenhouses and can heat domestic hot water, spas or swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 Manufacturer specifies for indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically, an aquastat that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 Particulate matter emissions are measured from a wood-fired hydronic heating appliance burning a prepared test fuel crib in a test facility maintained at a set of prescribed conditions. Procedures for determining burn rates, and particulate emissions rates and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.2 Other Standards

2.2.2.1 ASTM E2515–11—*Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17).

2.2.2.2 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances* (IBR, see §60.17).

3.0 Terminology

3.1 Definitions.

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load as specified in this test method.

3.1.4 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with Section 13.

3.1.5 Burn Rate—The rate at which test fuel is consumed in an appliance. Measured in pounds (lbs) or kilograms of wood (dry basis) per hour (lb/hr or kg/hr).

3.1.6 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.7 Test Fuel Charge—The collection of test fuel layers placed in the appliance at the start of the emission test run.

3.1.8 Test Fuel Layer—Horizontal arrangement of test fuel units.

3.1.9 Test Fuel Unit—One or more test fuel pieces with ¾ inch (19 mm) spacers attached to the bottom and to one side. If composed of multiple test fuel pieces, the bottom spacer may be one continuous piece.

3.1.10 Test Fuel Piece—A single 4 × 4 (4 ±0.25 inches by 4 ±0.25 inches) [100 ±6 mm by 100 ±6 mm] white or red oak wood piece cut to the length required.

3.1.11 Test Run—An individual emission test that encompasses the time required to consume the mass of the test fuel charge.

3.1.12 Overall Efficiency (SLM)—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method.

3.1.13 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the "dilution tunnel" method specified in ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions catch and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of appliance delivers heat through circulation of the heated liquid (water) from the appliance to a remote heat exchanger and back to the appliance. Measurements of the water temperature difference as it enters and exits the heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. The input is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Appliance operation is conducted on a hot-to-hot test cycle meaning that the appliance is brought to operating temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within predetermined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment. Four test categories are used. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's rated heat output capacity.

5.0 Significance and Use

5.1 The measurement of particulate matter emission rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the appliance under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C).

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification of liquid being heated.

6.6 Water Temperature Measurement—Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger. Must meet the calibration requirements specified in section 10.1.

6.7 Wood Moisture Meter—Calibrated electrical resistance meter capable of measuring test fuel moisture to within 1 percent moisture content. Must meet the calibration requirements specified in section 10.4.

6.8 Flue Gas Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see § 60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see § 60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement—Must meet the requirements of CSA B415.1–10 (IBR, see § 60.17), clauses 6.3.1 through 6.3.3.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances including all controls and accessories necessary for installation in the test facility. A full set of specifications and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a guide in the set-up and testing of the appliance.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±1.0 lb (0.5 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the tank, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses, electrical cables, and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger.

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semi-annually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 8, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST traceable methods at least once every 6 months.

10.4 Moisture Meter. The moisture meter shall be calibrated per the manufacturer's instructions and checked before each use.

10.5 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, the appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in sections 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium burn rate (Category II or III) for at least 10 hours for noncatalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the 4 × 4 piece length would be 36 inches (46 inches × 0.8 = 36.8 inches rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. Pieces are to be spaced ¾ inches (19 mm) apart on all faces. The first fuel layer may be assembled using fuel units consisting of multiple 4 × 4s consisting of single pieces with bottom and side spacers of 3 or more pieces if needed for a stable layer. The second layer may consist of fuel units consisting of no more than two pieces with spacers attached on the bottom and side. The top two layers of the fuel charge must consist of single pieces unless the fuel charge is only three layers. In that instance only the top layer must consist of single units. Three-quarter inch (19 mm) by 1.5 inch (38 mm) spacers shall be attached to the bottom of piece to maintain a ¾ inch (19 mm) separation. When a layer consists of two or more units of 4 × 4s an additional ¾ inch (19 mm) thick by 1.5 inch (38 mm) wide spacer shall be attached to the vertical face of each end of one 4 × 4, such that the ¾ inch (19 mm) space will be maintained when two 4 × 4 units or pieces are loaded side by side. In cases where a layer contains an odd number of 4 × 4s one piece shall not be attached, but shall have spacers attached in a manner that will provide for the ¾ inch (19 mm) space to be maintained (See Figure 1). Spacers shall be attached perpendicular to the length of the 4 × 4s such that the edge of the spacer is 1 ±0.25 inch from the end of the 4 × 4s in the previous layers. Spacers shall be red or white oak and will be attached with either nails (non-galvanized), brads or oak dowels. The use of kiln-dried wood is not allowed.

12.2.1 Using a fuel moisture meter as specified in section 6.7 of the test method, determine the fuel moisture for each test fuel piece used for the test fuel load by averaging at least five fuel moisture meter readings measured parallel to the wood grain. Penetration of the moisture meter insulated electrodes for all readings shall be ¼ the thickness of the fuel piece or 19 mm (¾ in.), whichever is lesser. One measurement from each of three sides shall be made at approximately 3 inches from each end and the center. Two additional measurements shall be made centered between the other three locations. Each individual moisture content reading shall be in the range of 18 to 28 percent on a dry basis. The average moisture content of each piece of test fuel shall be in the range of 19 to 25 percent. It is not required to measure the moisture content of the spacers. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture shall be measured within 4 hours of using the fuel for a test.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel Charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of standard fuel that most nearly match this target weight. This is the standard fuel charge for all tests. For example, if the firebox loading area volume is 10 ft^3 (280L) and the firebox depth is 46 inches (1168 mm), test fuel charge target is 100 lbs (45 kg) minimum and the piece length is 36 inches (914 mm). If eight 4 × 4s, 36 inches long weigh 105 lbs (48 kg), use 8 pieces for each test fuel charge. All test fuel charges will be of the same configuration.

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by ASTM E2515–11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content at the laboratories' discretion to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Pretest Burn Cycle. Reload appliance with oak wood and allow it to burn down to the specified coal bed weight. The pretest burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.1 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.2 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F. Aquastat or other heater output control device settings that are adjustable shall be set using manufacturer specifications, either as factory set or in accordance with the owner's manual, and shall remain the same for all burn categories.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.2, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of ASTM E2515 (IBR, see §60.17).

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3 (a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3 (g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3 (f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3 (i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3 (h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see §60.17), clauses 10.4.3 (a).

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger. If the heat output rate gets close to the upper or lower limit of the target range (±5 percent) adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0. 5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. The test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II, provided that the completed test run burn rate is no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

When the alternative heat output rate is used, the weightings for the weighted averages indicated in Table 2 shall be the average of the Category I and II weightings and shall be applied to both Category II results. The two completed runs in Category II will be deemed to meet the requirement for runs completed in both Category I and Category II. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method. The test report must include full documentation and discussion of the attempted runs, completed rums and calculations.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in burn rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in burn rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that burn rate Category I cannot be achieved. Note that section 12.5.6 requires that the completed test run burn rate can be no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

12.5.7 Appliance Overheating. Appliances shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3.1. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate (See section 14.1.14). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

E_T—Total particulate emissions for the full test run as determined per ASTM E2515–11 (IBR, see §60.17) in grams

$E_{g/MJ}$—Emissions rate in grams per megajoule of heat output
$E_{lb/mmBtu}$ output—Emissions rate in pounds per million Btu of heat output
$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned
$E_{g/hr}$—Emissions factor in grams per hour
HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg)
LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg)
ΔT—Temperature difference between water entering and exiting the heat exchanger
Q_{out}—Total heat output in BTU's (megajoules)
Q_{in}—Total heat input available in test fuel charge in BTU (megajoules)
M—Mass flow rate of water in lb/min (kg/min)
V_i—Volume of water indicated by a totalizing flow meter at the ith reading in gallons (liters)
V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min)
Θ—Total length of test run in hours
ti—Data sampling interval in minutes
η_{del}—Delivered heating efficiency in percent
Fi—Weighting factor for heat output category i (See Table 2)
T1—Temperature of water at the inlet on the supply side of the heat exchanger
T2—Temperature of the water at the outlet on the supply side of the heat exchanger
T3—Temperature of water at the inlet to the load side of the heat exchanger
TIavg—Average temperature of the appliance and water at start of the test

$$TI_{avg} - (T1 + T2)/2 \text{ at the start of the test, °F} \qquad \text{Eq.1}$$

TF_{avg}—Average temperature of the appliance and water at the end of the test

$$TF_{avg} - (T1 + T2)/2 \text{ at the end of the test, °F} \qquad \text{Eq.2}$$

MC—Fuel moisture content in percent dry basis
MC_i—Average moisture content of individual 4 × 4 fuel pieces in percent dry basis
MC_{sp}—Moisture content of spacers assumed to be 10 percent dry basis
σ—Density of water in pounds per gallon
C_p—Specific heat of water in Btu/lb, °F
C_{steel}—Specific heat of steel (0.1 Btu/lb, °F)
W_{fuel}—Fuel charge weight in pounds (kg)
W_i—Weight of individual fuel 4 × 4 pieces in pounds (kg)
W_{sp}—Weight of all spacers used in a fuel load in pounds (kg)
W_{app}—Weight of empty appliance in pounds
W_{wa}—Weight of water in supply side of the system in pounds

13.2 After the test is completed, determine the particulate emissions E_T in accordance with ASTM E2515–11 (IBR, see §60.17).

13.3 Determine Average Fuel Load Moisture Content

$$MC_{Ave} = [[\ \Sigma\ W_i \times MC_i\ ] + [\ W_{sp} \times MC_{sp}\ ]] \div W_{fuel}, \% \qquad \text{Eq. 3}$$

13.4 Determine heat input

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \times HHV, \text{ BTU} \qquad \text{Eq. 4}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \times LHV, \text{ BTU} \qquad \text{Eq. 5}$$

13.5 Determine Heat Output and Efficiency

13.5.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance.

$$Q_{out} = \left[\sum (C_{pi} \bullet \Delta T_i \bullet \dot{M}_i \bullet t_i)\right] + (W_{app} \bullet C_{Steel} + C_{pa} W_{water}) \bullet (TF_{avg} - TI_{avg}) \text{, BTU} \quad \text{Eq. 6}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.

M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min

$$M_i = V_{fi} \cdot \sigma_i \text{, lb/min} \quad \text{Eq. 7}$$

$$\Sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2))\ 0.1337 \text{, lbs/gal} \quad \text{Eq. 8}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, °F} \quad \text{Eq. 9}$$

C_{steel} = 0.1 Btu/lb, ° F

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2) \text{, Btu/lb-°F} \quad \text{Eq. 10}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}) \text{, gal/min} \quad \text{Eq. 11}$$

NOTE: Vi is the total water volume at the end of interval i and Vi-1 is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.5.2 Determine heat output rate as:

$$\text{Heat Output Rate} = Q_{out}/\Theta \text{, BTU/hr} \quad \text{Eq. 12}$$

13.5.3 Determine emission rates and emission factors as:

$$E_{g/MJ} = E_T/(Q_{out} \text{ x } 0.001055) \text{, g/MJ} \quad \text{Eq. 13}$$

$$E_{lb/MM\ BTU\ output} = (E_T/453.59)/(Q_{output} \text{ x } 10^{-6}) \text{, lb/mmBtu Out} \quad \text{Eq. 14}$$

$$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100)) \text{, g/dry kg} \quad \text{Eq, 15}$$

$$E_{g/hr} = E_T/\Theta \text{, g/hr} \quad \text{Eq. 16}$$

13.5.4 Determine delivered efficiency as:

$$\eta_{del} = (Q_{out}/Q_{in}) \text{ x } 100, \% \qquad \text{Eq. 17}$$

$$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \text{ x } 100, \% \qquad \text{Eq. 18}$$

13.5.5 Determine η_{SLM}—Overall Efficiency (SLM) using Stack Loss

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see § 60.17), clause 13.7 except for 13.7.2 (e), (f), (g), and (h), use the following average fuel properties for oak: percent C = 50.0, percent H = 6.6, percent O = 43.2, percent ash = 0.2 percent. The averaging period for determination of efficiency by the stack loss method allows averaging over 10 minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency. However, under some cycling conditions the ‘‘on’’ period may be short relative to this 10 minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, the averaging periods specified may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

13.5.5.1 Whenever the CSA B415.1–10 (IBR, see § 60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 16 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result.

13.6 Weighted Average Emissions and Efficiency

13.6.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (Fi) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ‘‘bin’’—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

$$\text{Weighted average delivered efficiency: } \eta_{avg} = \Sigma\ \eta_i \text{ x } F_i, \% \qquad \text{Eq. 19}$$

$$\text{Weighted average emissions: } E_{avg} = \Sigma E_i \text{ x } F_i, \% \qquad \text{Eq. 20}$$

13.7 Average Heat Output ($Q_{out\text{-}8hr}$) and Efficiency (($\eta_{avg\text{-}8hr}$) for 8 hour burn time.

13.7.1 Units tested under this standard typically require infrequent fuelling, 8 to 12 hours intervals being typical. Rating unit’s based on an average output sustainable over an 8 hour duration will assist consumers in appropriately sizing units to match the theoretical heat demand of their application.

13.7.2 Calculations:

$$Q_{out\text{-}8hr} = X1 + \{ (8 - Y1) \text{ x } [(X2 - X1) / (Y2 - Y1)] \}, \% \qquad \text{Eq. 21}$$

$$\eta_{avg\text{-}8hr} = \eta_{del1} + \{ (8 - Y1) \text{ x } [(\eta_{del2} - \eta_{del1}) / (Y2 - Y1)] \}, \% \qquad \text{Eq. 22}$$

Where:

Y1 = Test duration just above 8 hrs
Y2 = Test duration just below 8 hrs
X1 = Actual load for duration Y1
X2 = Actual load for duration Y2
η_{del1} = Average delivered efficiency for duration Y1
η_{del2} = Average delivered efficiency for duration Y2

13.7.2.1 Determine the test durations and actual load for each category as recorded in Table 1A.

13.7.2.2 Determine the data point that has the nearest duration greater than 8 hrs.

X1 = Actual load,
Y1 = Test duration, and
η_{del1} = Average delivered efficiency for this data point

13.7.2.3 Determine the data point that has the nearest duration less than 8 hours.

X2 = Actual load,
Y2 = Test duration, and
η_{del2} = Average delivered efficiency for this data point

13.7.2.4 Example:

CATEGORY ACTUAL LOAD DURATION

[Category Actual Load Duration ηdel]

(Btu/Hr)	(Hr)	(%)
1 15,000	10.2	70.0
2 26,000	8.4	75.5
3 50,000	6.4	80.1
4 100,000	4.7	80.9

Category 2 duration is just above 8 hours, therefore: X1 = 26,000 Btu/hr, η_{del1} = 75.5% and Y1 = 8.4 hrs

Category 3 duration is just below 8 hours, therefore: X2 = 50,000 Btu/hr, η_{del2} = 80.1% and Y2 = 6.4 hrs

$Q_{out\text{-}8hr}$ = 26,000 + {(8—8.4) × [(50,000—26,000)/(6.4—8.4)]} = 30,800 BTU/hr

$\eta_{avg\text{-}8hr}$ = 75.5 + {(8—8.4) × [(80.1—75.5)/(6.4—8.4)]} = 76.4%

13.8 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30\text{x}10^{-5} \qquad \text{Eq. 23}$$

Total CO emissions for each of the three test periods (CO_{-1}, CO_{-2}, CO_{-3}) shall be calculated as the sum of the emission rates for each of the 1 minute intervals.

Total CO emission for the test run, CO_T, shall be calculated as the sum of CO_{-1}, CO_{-2}, and CO_{-3}.

14.0 Report

14.1.1 The report shall include the following.

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A statement that the test results apply only to the specific appliance tested.

14.1.5 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.6 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.7 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.8 A list of participants and observers present for the tests.

14.1.9 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.10 Drawings and calculations used to determine firebox volume.

14.1.11 Information for each test run fuel charge including piece size, moisture content, and weight.

14.1.12 All required data for each test run shall be provided in spreadsheet format. Formulae used for all calculations shall be accessible for review.

14.1.13 Test run duration for each test.

14.1.14 Calculated results for delivered efficiency at each burn rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.15 Tables 1A, 1B, 1C and Table 2 must be used for presentation of results in test reports.

14.1.16 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.17 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in Method 28WHH because the appliance operation and fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this measurement method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in Method 28WHH for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters.

Table 1A. Data Summary Part A

						Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Act Load	Test Duration	Wood Wt	Wood Moisture	Heat Input	Heat Output
			BTU/hr	BTU/hr	% of max	hrs	lb	% DB	BTU	BTU
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	η_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp.	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	$lb_{MMBTU\ Out}$	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

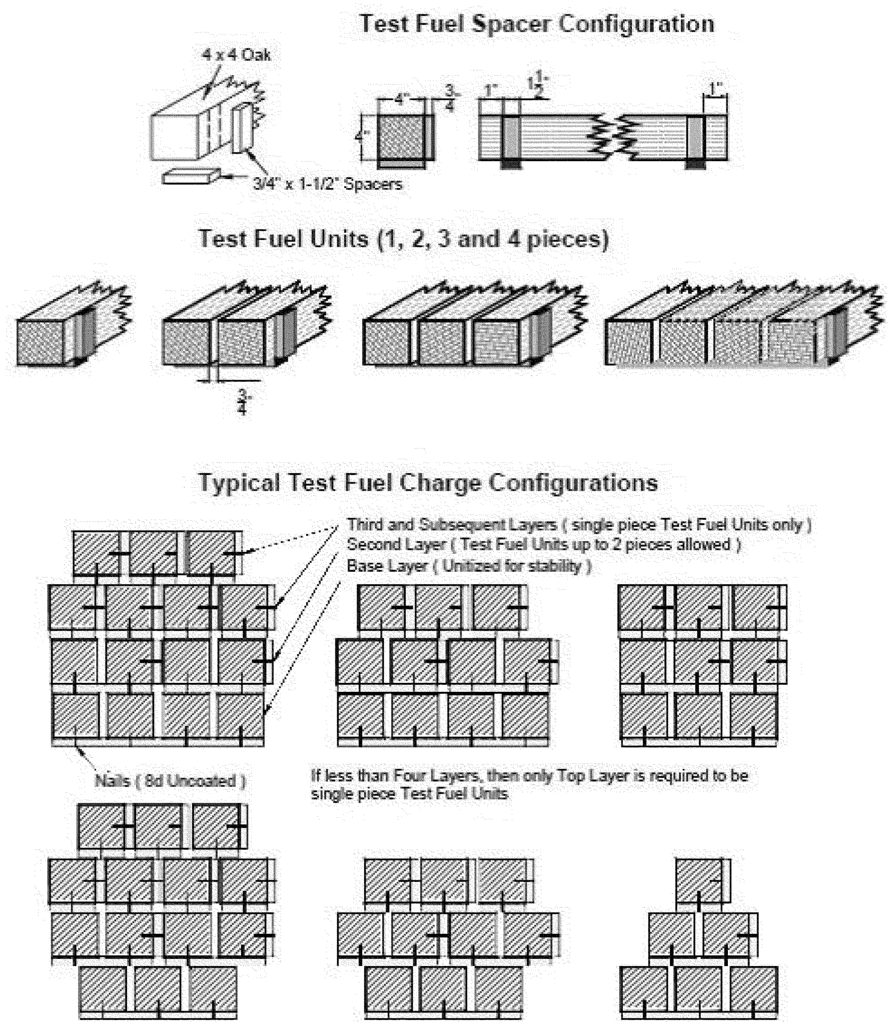
Table 1C: Hangtag Information (optional)

MANUFACTURER:			
MODEL NUMBER:			
MAXIMUM OUTPUT RATING:	Qmax		BTU/HR
ANNUAL EFFICIENCY RATING:	η_{avg}		(Using higher heating value)
PARTICLE EMISSIONS:	E_{avg}		GRAMS/HR (average)
			LBS/MILLION BTU OUTPUT
CARBON MONOXIDE:	COg/MIN		GRAMS/MINUTE

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i}$ x F_i	$E_{g/MJ,i}$ x F_i	$E_{g/kg,i}$ x F_i	$E_{lb/mmBtu\ Out,i}$ x F_i	$E_{g/hr,i}$ x F_i
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Typical Test Fuel Piece



TEST METHOD 28WHH FOR CERTIFICATION OF CORD WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE: MEASUREMENT OF PARTICULATE MATTER (PM) AND CARBON MONOXIDE (CO) EMISSIONS AND HEATING EFFICIENCY OF WOOD-FIRED HYDRONIC HEATING APPLIANCES WITH PARTIAL THERMAL STORAGE

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances with heat storage external to the appliance. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture. Throughout this document, the term ''water'' will be used to denote any of the heat transfer liquids approved for use by the manufacturer.

1.2 The test method measures PM and CO emissions and delivered heating efficiency at specified heat output rates referenced against the appliance's rated heating capacity as specified by the manufacturer and verified under this test method.

1.3 PM emissions are measured by the dilution tunnel method as specified in the EPA Method 28WHH and the standards referenced therein with the exceptions noted in section 12.5.9. Delivered efficiency is measured by determining the fuel energy input and appliance output. Heat output is determined through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and the increase in energy of the external storage. Heat input is determined from the mass of dry wood fuel and its higher heating value (HHV). Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized hydronic heating appliances intended to be fired with wood and for which the manufacturer specifies for indoor or outdoor installation. The system, which includes the heating appliance and external storage, is commonly connected to a heat exchanger by insulated pipes and normally includes a pump to circulate heated liquid. These systems are used to heat structures such as homes, barns and greenhouses. They also provide heat for domestic hot water, spas and swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 The manufacturer specifies the application for either indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically an aquastat mounted as part of the appliance that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is available in the firebox. The appliance may be equipped with other devices to control combustion.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.5.5 A liquid storage system, typically water, which is not large enough to accept all of the heat produced when a full load of wood is burned and the storage system starts a burn cycle at 125 °F.

1.5.6 The heating appliances require external thermal storage and these units will only be installed as part of a system which includes thermal storage. The manufacturer specifies the minimum amount of thermal storage required. However, the storage system shall be large enough to ensure that the boiler (heater) does not cycle, slumber, or go into an off-mode when operated in a Category III load condition (See section 4.3).

1.6 The values stated are to be regarded as the standard whether in I–P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 PM and CO emissions are measured from a wood–fired hydronic heating appliance burning a prepared test fuel charge in a test facility maintained at a set of prescribed conditions. Procedures for determining heat output rates, PM and CO emissions, and efficiency and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.1.2 Method 28WHH Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances and the Standards Referenced therein.

2.2.2 Other Standards

2.2.2.1 CSA–B415.1–10 *Performance Testing of Solid-Fuel-Burning Heating Appliances*

3.0 Terminology

3.1 Definitions

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load or the storage system as specified in this test method.

3.1.4 Emission Factor—The emission of a pollutant expressed in mass per unit of energy (typically) output from the boiler/heater.

3.1.5 Emission Index—The emission of a pollutant expressed in mass per unit mass of fuel used.

3.1.6 Emission Rate—The emission of a pollutant expressed in mass per unit time

3.1.7 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with section 12.5.4.

3.1.8 Heat Output Rate—The average rate of energy output from the appliance during a specific test period in Btu/hr (MJ/hr).

3.1.9 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.10 NIST—National Institute of Standards and Technology.

3.1.11 Test Fuel Charge—The collection of test fuel placed in the appliance at the start of the emission test run.

3.1.12 Test Run—An individual emission test which encompasses the time required to consume the mass of the test fuel charge. The time of the test run also considers the time for the energy to be drawn from the thermal storage.

3.1.13 Test Run Under "Cold-to-Cold" Condition—Under this test condition the test fuel is added into an empty chamber along with kindling and ignition materials (paper). The boiler/heater at the start of this test is typically 125° to 130 °F.

3.1.14 Test Run Under "Hot-to-Hot" Condition—Under this test condition the test fuel is added onto a still-burning bed of charcoals produced in a pre-burn period. The boiler/heater water is near its operating control limit at the start of the test.

3.1.15 Overall Efficiency, also known as Stack Loss Efficiency—The efficiency for each test run as determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method (SLM).

3.1.16 Phases of a Burn Cycle—The "startup phase" is defined as the period from the start of the test until 15 percent of the test fuel charge is consumed. The "steady-state phase" is defined as the period from the end of the startup phase to a point at which 80 percent of the test fuel charge is consumed. The "end phase" is defined as the time from the end of the steady-state period to the end of the test.

3.1.17 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

3.1.18 Slumber Mode—This is a mode in which the temperature of the water in the boiler/heater has exceeded the operating control limit and the control has changed the boiler/heater fan speed, dampers, and/or other operating parameters to minimize the heat output of the boiler/heater.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the "dilution tunnel" method specified in EPA Method 28WHH and the standards referenced therein. The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions collected and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of system delivers heat through circulation of the heated liquid (water) from the system to a remote heat exchanger (*e.g.* baseboard radiators in a room) and back to the system. Measurements of the cooling water temperature difference as it enters and exits the test system heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. Also included in the heat output is the change in the energy content in the storage system during a test run. Energy input to the appliance during the test run is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1–10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Four test categories are defined for use in this method. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's Rated Heat Output Capacity. These heat output categories refer to the output from the system by way of the load heat exchanger installed for the test. The output from just the boiler/heater part of the system may be higher for all or part of a test, as part of this boiler/heater output goes to storage.

For the Category III and IV runs, appliance operation is conducted on a hot-to-hot test cycle meaning that the appliance is brought to operating temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within pre-determined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment.

For the Category I and II runs, the unit is tested with a ‘‘cold start.’’ At the manufacturer's option, the Category II and III runs may be waived and it may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

All test operations and measurements shall be conducted by personnel of the laboratory responsible for the submission of the test report.

5.0 Significance and Use

5.1 The measurement of particulate matter emission and CO rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the boiler/heater under test and associated parts and accessories when completely filled with water to an accuracy of ±1.0 pound (±0.5 kg) and a readout resolution of ±0.2 pound (±0.1 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type—T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ±0.50 °F (±0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ±0.50 °F (±0.25 °C). This measurement uncertainty shall include the temperature sensor, sensor well arrangement, piping arrangements, lead wire, and measurement/recording system. The response time of the temperature measurement system shall be less than half of the time interval at which temperature measurements are recorded.

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ±1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ±1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification, in the boiler/heater, of liquid being heated.

6.6 Water Temperature Measurement. Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger must meet the calibration requirements specified in 10.1 of this method.

6.7 Lab Scale. For measuring the moisture content of wood slices as part of the overall wood moisture determination. Accuracy of ±0.01 pounds.

6.8 Flue Gas Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see § 60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see § 60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement. Must meet the requirements of CSA B415.1–10 (IBR, see § 60.17), clauses 6.3.1 through 6.3.3.

6.11 Dilution Tunnel CO Measurement. In parallel with the flue gas composition measurements, the CO concentration in the dilution tunnel shall also be measured and reported at time intervals not to exceed one minute. This analyzer shall meet the zero and span drift requirements of CSA B415.1–10 (IBR, see § 60.17). In addition the measurement repeatability shall be better than ±15 ppm over the range of CO levels observed in the dilution tunnel.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances, as described in marketing materials, including all controls and accessories necessary for installation in the test facility. A full set of specifications, installation and operating instructions, and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a guide in the set-up and testing of the appliance and shall be part of the test record.

8.2 The size, connection arrangement, and control arrangement for the thermal storage shall be as specified in the manufacturer's documentation. It is not necessary to use the specific storage system that the boiler/heater will be marketed with. However, the capacity of the system used in the test cannot be greater than that specified as the minimum allowable for the boiler/heater.

8.3 All system control settings shall be the as-shipped, default settings. These default settings shall be the same as those communicated in a document to the installer or end user. These control settings and the documentation of the control settings as to be provided to the installer or end user shall be part of the test record.

8.4 Where the manufacturer defines several alternatives for the connection and loading arrangement, one shall be defined in the appliance documentation as the default or standard installation. It is expected that this will be the configuration for use with a simple baseboard heating system. This is the configuration to be followed for these tests. The manufacturer's documentation shall define the other arrangements as optional or alternative arrangements.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ±0.2 lb (0.1 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ±0.5 feet (4.6 ±0.15 m) from the upper surface of the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ±0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the boiler/heater with water, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses and electrical cables and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile (or equivalent instrumentation) meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TF_{avg} and TI_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Storage Tank. The storage tank shall include a destratification pump as illustrated in Figure 1. The pump will draw from the bottom of the tank and return to the top as illustrated. Temperature sensors (TS1 and TS2 in Figure 1) shall be included to measure the temperature in the recirculation loop. The valve plan in Figure 1 allows the tank recirculation loop to operate and the boiler/heater-to-heat exchanger loop to operate at the same time but in isolation. This would typically be done before the start of a test or following completion of a test to determine the end of test average tank temperature. The nominal flow rate in the storage tank recirculation loop can be estimated based on pump manufacturers' performance curves and any significant restriction in the recirculation loop.

9.7 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semi-annually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST-traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 12, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST-traceable methods at least once every 6 months.

10.4 Flue Gas Analyzers—In accordance with CSA B415.1–10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, an appliance is to be operated for a minimum of 50 hours using a medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in section 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium heat output rate (Category II or III) for at least 10 hours for non-catalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus Alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the piece length would be 36 inches (46 inches × 0.8 = 36.8 inches, rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. The test fuel shall be cord wood with cross section dimensions and weight limits as defined in CSA B415.1–10 (IBR, see §60.17), section 8.3, Table 4. The use of dimensional lumber is not allowed.

12.2.1 Select three pieces of cord wood from the same batch of wood as the test fuel and the same weight as the average weight of the pieces in the test load ±1.0 lb. From each of these three pieces, cut three slices. Each slice shall be ½ inch to ¾ inch thick. One slice shall be cut across the center of the length of the piece. The other two slices shall be cut half way between the center and the end. Immediately measure the mass of each piece in pounds. Dry each slice in an oven at 220 °F for 24 hours or until no further weight change occurs. The slices shall be arranged in the oven so as to provide separation between faces. Remove from the oven and measure the mass of each piece again as soon as practical, in pounds.

The moisture content of each slice, on a dry basis, shall be calculated as:

$$MC_{slice} = \frac{100 \cdot (W_{SliceWet} - W_{SliceDry})}{W_{SliceDry}}$$

Where:

$W_{SliceWet}$ = weight of the slice before drying in pounds

$W_{SliceDry}$ = weight of the slice after drying in pounds

MC_{Slice} = moisture content of the slice in % dry basis

The average moisture content of the entire test load (MC) shall be determined using Eq. 6. Each individual slice shall have a moisture content in the range of 18 percent to 28 percent on a dry basis. The average moisture content for the test fuel load shall be in the range of 19 percent to 25 percent. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture measurement shall begin within 4 hours of using the fuel batch for a test. Use of a pin-type meter to estimate the moisture content prior to a test is recommended.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft^3 (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of cord wood that most nearly match this target weight. However, the test fuel charge cannot be less than the target of 10 pounds (4.54 kg) per ft^3 (28L).

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by EPA Method 28WHH and the standards referenced therein.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content, at the laboratory's discretion, to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Startup Procedure for Category III and IV Test Runs, "Hot-to-Hot."

12.4.1.1 Pretest t Burn Cycle. Following appliance startup (section 12.4), reload appliance with oak cord wood and allow it to burn down to the specified coal bed weight. The pre-test burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoalization is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoalization is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoalization while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.2 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoalization. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.1.3 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.4.1.4 Storage. The Category III and IV test runs may be done either with or without the thermal storage. If thermal storage is used, the initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. If thermal storage is used, prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6). If the Category III and IV runs are done with storage, it is recognized that during the last hour of the preburn cycle the storage tank must be mixed to achieve a uniform starting temperature and cannot receive heat from the boiler/heater during this time. During this time period, the boiler/heater might cycle or go into a steady reduced output mode. (Note—this would happen, for example, in a Category IV run if the actual maximum output of the boiler/heater exceed the manufacturer's rated output.) A second storage tank may be used temporarily to enable the boiler/heater to operate during this last hour of the preburn period as it will during the test period. The temperature of this second storage tank is not used in the calculations but the return water to the boiler/heater (after mixing device if used) must be 125 °F or greater.

12.4.2 Startup Procedure for Category I and II Test Runs, ''Cold-to-Cold.''

12.4.2.1 Initial Temperatures. This test shall be started with both the boiler/heater and the storage at a minimum temperature of 125 °F. The boiler/heater maximum temperature at the start of this test shall be 135 °F. The boiler/heater and storage may be heated through a pre-burn or it may be heated by external means.

12.4.2.2 Firebox Condition at Test Start. Prior to the start of this test remove all ash and charcoal from the combustion chamber(s). The loading of the test fuel and kindling should follow the manufacturer's recommendations, subject to the following constraints: Up to 10 percent kindling and paper may be used which is in addition to the fuel load. Further, up to 10 percent of the fuel load (*i.e.*, included in the 10 lb/ft^3) may be smaller than the main fuel. This startup fuel shall still be larger than 2 inches.

12.4.2.3 Storage. The Category I and II test runs shall be done with thermal storage. The initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pretest burn cycle or it may be heated by external means. Prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS_1 and TS_2) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F (this is lower than the initial tank temperature to allow for any pipeline losses). Where the storage system is used, flow of water from the boiler/heater shall be divided between the storage tank and the heat exchanger such that the temperature change of the circulating water across the heat exchanger shall be 30 ±5 °F, averaged over the entire test run. This is typically adjusted using the system valves.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. For Category III and IV runs: Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.1, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

For Category I and II runs: Once the appliance has reached the starting temperature, tare the scale and load the full test charge, including kindling into the appliance. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Light the fire following the manufacturer's written normal startup procedure. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of EPA Method 28WHH and the standards referenced therein.

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1–10 (IBR, see § 60.17) clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3(a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1–10 (IBR, see § 60.17), clauses 6.2.1, 8.5.7 and 10.4.3(g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1–10 (IBR, see § 60.17), clauses 6.2.2, 8.5.7 and 10.4.3(f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO_2) concentrations in the flue gas in accordance with CSA B415.1–10 (IBR, see § 60.17), clauses 6.3, 8.5.7 and 10.4.3(i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1–10 (IBR, see § 60.17), clauses 8.5.7 and 10.4.3(h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1–10 (IBR, see § 60.17), clause 10.4.3(a).

12.5.1.3.6 Record and document all settings and adjustments, if any, made to the boiler/heater as recommended/required by manufacturer's instruction manual for different combustion conditions or heat loads. These may include temperature setpoints, under and over-fire air adjustment, or other adjustments that could be made by an operator to optimize or alter combustion. All such settings shall be included in the report for each test run.

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger based on water temperatures and flow. If the heat output rate over a 10 minute averaging period gets close to the upper or lower limit of the target range (±5 percent), adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0.5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. For the Category III and IV, ''hot-to-hot'' test runs, the test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). ($W_{FuelBurned} = W_{fuel}$) End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

For the Category I and II ''cold-to-cold'' test runs, the test run is completed; and the end of a test is defined at the first occurrence of any one of the following:

(a) The remaining weight of the test fuel charge is less than 1 percent of the total test fuel weight ($W_{FuelBurned} > 0.99 \cdot W_{fuel}$);

(b) The automatic control system on the boiler/heater switches to an off mode. In this case, the boiler/heater fan (if used) is typically stopped and all air flow dampers are closed by the control system. Note that this off mode cannot be an ''overheat'' or emergency shutdown which typically requires a manual reset; or

(c) If the boiler/heater does not have an automatic off mode: After 90 percent of the fuel load has been consumed and the scale has indicated a rate of change of the test fuel charge of less than 1.0 lb/hr for a period of 10 minutes or longer. Note—this is not considered ''stopped fuel combustion,'' See section 12.5.6.1.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.3.2 At the end of the test run, continue to operate the storage tank destratification pump until the total volume pumped exceeds 1.5 times the tank volume. The maximum average of the top and bottom temperatures measured after this time may be taken as the average tank temperature at the end of the tests (TFSavg, See section 13.1). The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5.3.3 For the Category I and II test runs, there is a need to determine the energy content of the unburned fuel remaining in the chamber if the remaining mass in the chamber is greater than 1 percent of the test fuel weight. Following the completion of the test, as soon as safely practical, this remaining fuel is removed from the chamber, separated from the remaining ash and weighed. This separation could be implemented with a slotted ''scoop'' or similar tool. A ¼ inch opening size in the separation tool shall be used to separate the ash and charcoal. This separated char is assigned a heating value of 12,500 Btu/lb.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer. Alternatively, during the Category IV run, if the rated output cannot be maintained for a 15 minute interval, the manufacturer may elect to reduce the rated output to match the test and complete the Category IV run on this basis. The target outputs for Categories I, II, and III shall then be recalculated based on this change in rated output capacity.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II. When this is the case, the weightings for the weighted averages indicated in section 14.1.15 shall be the average of the Category I and II weighting's and shall be applied to both Category II results. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in heat output rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in heat output rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that heat output rate Category I cannot be achieved.

12.5.7 Appliance Overheating. Appliances with their associated thermal storage shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control—typically requires manual reset), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.5.8 Option to Eliminate Tests in Category II and III. Following successful completion of a test run in Category I, the manufacturer may eliminate the Category II and III tests. For the purpose of calculating the annual averages for particulates and efficiency, the values obtained in the Category I run shall be assumed to apply also to Category II and Category III. It is envisioned that this option would be applicable to systems which have sufficient thermal storage such that the fuel load in the Category I test can be completely consumed without the system reaching its upper operating temperature limit. In this case, the boiler/heater would likely be operating at maximum thermal output during the entire test and this output rate may be higher than the manufacturer's rated heat output capacity. The Category II and III runs would then be the same as the Category I run. It may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III, for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

12.5.9 Modification to Measurement Procedure in EPA Method 28WHH to Determine Emissions Separately During the Startup, Steady-State and End Phases. With one of the two particulate sampling trains used, filter changes shall be made at the end of the startup phase and the steady-state phase (See section 3.0). This shall be done to determine the particulate emission rate and particulate emission index for the startup, steady-state, and end phases individually. For this one train, the particulates measured during each of these three phases shall be added together to also determine the particulate emissions for the whole run.

12.5.10 Modification to Measurement Procedure in EPA Method 28WHH and the Standards Referenced therein on Averaging Period for Determination of Efficiency by the Stack Loss Method. The methods currently defined in Method 28WHH allow averaging over 10-minute time periods for flue gas temperature, flue gas CO_2, and flue gas CO for the determination of the efficiency with the stack loss method. However, under some cycling conditions the ''on'' period may be short relative to this 10-minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, averaging periods as specified in EPA Method 28WHH and the standards referenced therein, may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate. The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

CO_s—Carbon monoxide measured in the dilution tunnel at arbitrary time in ppm dry basis.

$CO_{g/min}$—Carbon monoxide emission rate in g/min.

CO_T—Total carbon monoxide emission for the full test run in grams.

CO_{-1}—Startup period carbon monoxide emissions in grams.

CO_{-2}—Steady-state period carbon monoxide emission in grams.

CO_{-3}—End period carbon monoxide emission in grams.

E_T—Total particulate emissions for the full test run as determined per EPA Method 28WHH and the standards referenced therein in grams.

E_1—Startup period particulate emissions in grams.

E_2—Steady-state period particulate emissions in grams.

E_3—End period particulate emissions in grams.

$E_{1-g/kg}$—Startup period particulate emission index in grams per kg fuel.

$E_{2-g/kg}$—Steady-state period particulate emission index in grams per kg fuel.

$E_{3-g/kg}$—End period particulate emission index in grams per kg fuel.

$E_{1-g/hr}$—Startup period particulate emission rate in grams per hour.

$E_{2-g/hr}$—Steady-state period particulate emission rate in grams per hour.

$E_{3-g/hr}$—End period particulate emission rate in grams per hour.

$E_{g/MJ}$—Emission rate in grams per MJ of heat output.

$E_{lb/mmBtu\ output}$—Emissions rate in pounds per million Btu of heat output.

$E_{g/kg}$—Emissions factor in grams per kilogram of dry fuel burned.

$E_{g/hr}$—Emission factor in grams per hour.

HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg).

LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg).

ΔT—Temperature difference between cooling water entering and exiting the heat exchanger.

Q_{out}—Total heat output in Btu (MJ).

Q_{in}—Total heat input available in test fuel charge in Btu's (MJ).

Q_{std}—Volumetric flow rate in dilution tunnel in dscfm.

M—Mass flow rate of water in lb/min (kg/min).

V_i—Volume of water indicated by a totalizing flow meter at the i_{th} reading in gallons (liters).

V_f—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min).

Θ—Total length of burn period in hours ($\Theta_1 + \Theta_2 + \Theta_3$).

Θ_1—Length of time of the startup period in hours.

Θ_2—Length of time of the steady-state period in hours.

Θ_3—Length of time of the end period in hours.

Θ_4—Length of time for stored heat to be used following a burn period in hours.

t_i—Data sampling interval in minutes.

η_{del}—Delivered heating efficiency in percent.

F_i—Weighting factor for heat output category i. (See Table 2.)

T1—Temperature of water at the inlet on the supply side of the heat exchanger, °F.

T2—Temperature of the water at the outlet on the supply side of the heat exchanger, °F.

T3—Temperature of cooling water at the inlet to the load side of the heat exchanger, °F.

T4—Temperature of cooling water at the outlet of the load side of the heat exchanger, °F.

T5—Temperature of the hot water supply as it leaves the boiler/heater, °F.

T6—Temperature of return water as it enters the boiler/heater, °F.

T7—Temperature in the boiler/heater optional destratification loop at the top of the boiler/heater, °F.

T8—Temperature in the boiler/heater optional destratification loop at the bottom of the boiler/heater, °F.

TI_{avg}—Average temperature of the appliance and water at start of the test.

$$TI_{avg} - (T5 + T6)/2 \text{ at the start of the test, °F.} \qquad \text{Eq. 1}$$

TF_{avg}—Average temperature of the appliance and water at the end of the test.

$$TF_{avg} - (T5 + T6)/2 \text{ at the end of the test, °F.} \qquad \text{Eq. 2}$$

TIS_1—Temperature at the inlet to the storage system at the start of the test.

TIS_2—Temperature at the outlet from the storage system at the start of the test.

TFS_1—Temperature at the inlet to the storage system at the end of the test.

TFS_2—Temperature at the outlet from the storage system at the end of the test.

TIS_{avg}—Average temperature of the storage system at the start of the test.

$$TIS_{avg} - (TIS_1 + TIS_2)/2 \text{ at the end of the test.} \qquad \text{Eq. 3}$$

TFS_{avg}—Average temperature of the storage system at the end of the test.

$$TFS_{avg} - (TFS_1 + TFS_2)/2. \qquad \text{Eq. 4}$$

MC—Fuel moisture content in percent dry basis.

σ—Density of water in pounds per gallon.

$\sigma_{Initial}$—Density of water in the boiler/heater system at the start of the test in pounds per gallons.

$\sigma_{boiler/heater}$—Density of water in the boiler/heater system at an arbitrary time during the test in pounds per gallon.

C_p—Specific heat of water in Btu/lb, °F.

C_{steel}—Specific heat of steel (0.1 Btu/lb, °F).

$V_{boiler/heater}$—total volume of water in the boiler/heater system on the weight scale in gallons.

W_{fuel}—Fuel charge weight, as-fired or ‘‘wet’’, in pounds (kg).

$W_{fuel—1}$—Fuel consumed during the startup period in pounds (kg).

$W_{fuel—2}$—Fuel consumed during the steady state period in pounds (kg).

$W_{fuel—3}$—Fuel consumed during the end period in pounds (kg).

$W_{FuelBurned}$—Weight of fuel that has been burned from the start of the test to an arbitrary time, including the needed correction for the change in density and weight of the water in the boiler/heater system on the scale in pounds (kg).

$W_{RemainingFuel}$—Weight of unburned fuel separated from the ash at the end of a test. Useful only for Category I and Category II tests.

W_{app}—Weight of empty appliance in pounds (kg).

W_{wat}—Weight of water in supply side of the system in pounds (kg).

$W_{ScaleInitial}$—Weight reading on the scale at the start of the test, just after the test load has been added in pounds (kg).

W_{Scale}—Reading of the weight scale at an arbitrary time during the test run in pounds (kg).

$W_{StorageTank}$—Weight of the storage tank empty in pounds (kg).

$W_{WaterStorage}$—Weight of the water in the storage tank at TIS_{avg} in pounds (kg).

13.2 After the test is completed, determine the particulate emissions E_T in accordance with EPA Method 28WHH and the standards referenced therein.

13.3 Determination of the weight of fuel that has been burned at an arbitrary time.

For the purpose of tracking the consumption of the test fuel load during a test run the following may be used to calculate the weight of fuel that burned since the start of the test:

$$W_{FuelBurned} = (W_{ScaleInitial} - W_{Scale}) + V_{Boiler/heater} \cdot (\sigma_{Initial} - \sigma_{boiler/heater}) \qquad \text{Eq. 5}$$

Water density, σ, is calculated using Equation 12.

13.4 Determine Average Fuel Load Moisture Content.

$$MC = \frac{\sum W_{SliceWet\_i} - MC_{Slice\_i}}{\sum W_{SliceWet\_i}} \qquad \text{Eq. 6}$$

13.5 Determine Heat Input.

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \text{ x HHV, Btu (MJ).} \qquad \text{Eq. 7}$$

$$Q_{in\ LHV} = (W_{fuel}/(1+(MC/100))) \text{ x LHV, Btu (MJ).} \qquad \text{Eq. 8}$$

13.5.1 Correction to Q_{in} for the Category I and II tests, where there is greater than 1 percent of the test fuel charge in the chamber at the end of the test period.

$$Q_{InCorrected} = Q_{in} - W_{Remaining} \cdot 12{,}500\ \underline{Btu} \qquad \text{Eq. 9}$$

13.6 Determine Heat Output, Efficiency, and Emissions.

13.6.1 Determine heat output as:

Q_{out} = Σ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance + Change in heat in storage tank.

$$Qout = \Sigma[C_{pi} \cdot \Delta T_i \cdot M_i \cdot t_i] + (W_{app} \cdot C_{steel} + W_{water} \cdot C_{pa}) \cdot (TF_{avg} - TI_{avg})$$

$$+ (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg}) \text{ Btu (MJ)} \qquad \text{Eq. 10}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i.M_i = Mass flow rate = gal/min × density of water (lb/gal) = lb/min.

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min.} \qquad \text{Eq. 11}$$

$$\sigma_i = (62.56 + (-.0003413 \text{ x } T3_i) + (-.00006225 \text{ x } T3_i^2))\ 0.1337, \text{ lb/gal.} \qquad \text{Eq. 12}$$

$$C_p = 1.0014 + (-.000003485 \text{ x } T3_i) \text{ Btu/lb, -°F.} \qquad \text{Eq. 13}$$

C_{steel} = 0.1 Btu/lb, -° F.

$$C_{pa} = 1.0014 + (-.000003485 \text{ X } (TI_{avg} + TF_{avg})/2), \text{ Btu/lb, °F.} \qquad \text{Eq. 14}$$

$$V_{fi} = (V_i - V_{i-1})/(t_i - t_{i-1}), \text{ gal/min.} \qquad \text{Eq. 15}$$

NOTE: V_i is the total water volume at the end of interval i and V_{i-1} is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.6.2 Determine Heat Output Rate Over Burn Period ($\Theta_1 + \Theta_2 + \Theta_3$) as:

$$\text{Heat Output Rate} = Q_{out}/\Theta,\ \text{Btu/hr (MJ/hr).} \qquad \text{Eq. 16}$$

13.6.3 Determine Emission Rates and Emission Factors as:

$$E_{g/MJ} = E_T/(Q_{out} \text{ x } 0.001055),\ \text{g/MJ.} \qquad \text{Eq. 17}$$

$$E_{lb/MM\ Btu\ output} = (E_T/453.59)/(Q_{out} \text{ x } 10^{-6}),\ \text{lb/mmBtu out.} \qquad \text{Eq. 18}$$

$$E_{g/kg} = E_T/(W_{fuel}/(1+MC/100)),\ \text{g/dry kg.} \qquad \text{Eq. 19}$$

$$E_{g/hr} = E_T/(\Theta_1 + \Theta_2 + \Theta_3 + \Theta_4),\ \text{g/hr.} \qquad \text{Eq. 20}$$

$$\Theta_4 = (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg})/(Q_{out}/\Theta) \qquad \text{Eq. 21}$$

If thermal storage is not used in a Category III or IV run, then $\Theta_4 = 0$.

$E_{1\text{—}g/kg} = E_1/(W_{fuel\text{—}1}/(1 + MC/100))$, g/dry kg.
$E_{2\text{—}g/kg} = E_2/(W_{fuel\text{—}2}/(1 + MC/100))$, g/dry kg.
$E_{3\text{—}g/kg} = E_3/(W_{fuel\text{—}3}/(1 + MC/100))$, g/dry kg.
$E_{1\text{—}g/hr} = E_1/\Theta_1$, g/hr.
$E_{2\text{—}g/hr} = E_2/\Theta_2$, g/hr.
$E_{3\text{—}g/hr} = E_3/\Theta_3$, g/hr.

13.6.4 Determine delivered efficiency as:

$$\eta_{del} = (Q_{out}/Q_{InCorrected}) \text{ x } 100,\ \%. \qquad \text{Eq. 22}$$

$$\eta_{del\ LHV} = (Q_{out}/Q_{in\ LHV}) \text{ x } 100,\ \%. \qquad \text{Eq. 23}$$

13.6.5 Determine η_{SLM}—Overall Efficiency, also known as Stack Loss Efficiency, using stack loss method (SLM).

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1–10 (IBR, see §60.17), clause 13.7 except for 13.7.2(e), (f), (g), and (h), use the following average fuel properties for oak: %C = 50.0, %H = 6.6, %O = 43.2, %Ash = 0.2.

13.6.5.1 Whenever the CSA B415.1–10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 22 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result. For a test where the CSA B415.1–10 overall efficiency SLM is less than 2 percentage points lower than the overall efficiency based on load side measurements, the efficiency based on load side measurements shall be considered invalid. [Note on the rationale for the 2 percentage points limit. The SLM method does not include boiler/heater jacket losses and, for this reason, should provide an efficiency which is actually higher than the efficiency based on the energy input and output measurements or ‘‘delivered efficiency.’’ A delivered efficiency that is higher than the efficiency based on the SLM could be considered suspect. A delivered efficiency greater than 2 percentage points higher than the efficiency based on the SLM, then, clearly indicates a measurement error.]

13.6.6 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30\text{x}10^{-5} \qquad \text{Eq. 24}$$

Total CO emissions for each of the three test periods ($CO_{\text{—}1}$, $CO_{\text{—}2}$, $CO_{\text{—}3}$) shall be calculated as the sum of the emission rates for each of the 1-minute intervals. Total CO emission for the test run, CO_T, shall be calculated as the sum of $CO_{\text{—}1}$, $CO_{\text{—}2}$, and $CO_{\text{—}3}$.

13.7 Weighted Average Emissions and Efficiency.

13.7.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (F_i) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or ''bin''—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

Weighted average delivered efficiency: $\eta_{avg} = \Sigma\, \eta_i \text{ x } F_i$, %. Eq. 25

Weighted average emissions: $E_{avg} = \Sigma\, E_i \text{ x } F_i$, % Eq. 26

If, as discussed in section 12.5.8, the option to eliminate tests in Category II and III is elected, the values of efficiency and particulate emission rate as measured in Category I, shall be assigned also to Category II and III for the purpose of determining the annual averages.

14.0 Report

14.1.1 The report shall include the following:

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A description of the minimum amount of external thermal storage that is required for use with this system. This shall be specified both in terms of volume in gallons and stored energy content in Btu with a storage temperature ranging from 125 °F to the manufacturer's specified setpoint temperature.

14.1.5 A statement that the test results apply only to the specific appliance tested.

14.1.6 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.7 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.8 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.9 A list of participants and their roles and observers present for the tests.

14.1.10 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.11 Drawings and calculations used to determine firebox volume.

14.1.12 Information for each test run fuel charge including piece size, moisture content and weight.

14.1.13 All required data and applicable blanks for each test run shall be provided in spreadsheet format both in the printed report and in a computer file such that the data can be easily analyzed and calculations easily verified. Formulas used for all calculations shall be accessible for review.

14.1.14 For each test run, Θ_1,Θ_2, Θ_3, the total CO and particulate emission for each of these three periods, and Θ_4.

14.1.15 Calculated results for delivered efficiency at each heat output rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.16 Tables 1A, 1B, 1C, 1D, 1E and Table 2 must be used for presentation of results in test reports.

14.1.17 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.18 A plot of CO emission rate in grams/minute vs. time, based on 1 minute averages, for the entire test period, for each run.

14.1.19 A plot of estimated boiler/heater energy release rate in Btu/hr based on 10 minute averages, for the entire test period, for each run. This will be calculated from the fuel used, the wood heating value and moisture content, and the SLM efficiency during each 10 minute period.

14.1.20 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in this test method because the appliance operation and fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this test method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in this test method for measuring solid fuel burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters, partial thermal storage.

Table 1A. Data Summary Part A

						Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Actual Load	Test Duration	Wood Weight as-fired	Wood Moisture	Heat Input	Heat Output
		Btu/hr	Btu/hr	Btu/hr	% of max	hrs	lb	%DB	Btu	Btu
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	H_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp.	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			°F	g	lb/mm Btu Out	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1C. Data Summary Part C

			Θ_1	Θ_2	Θ_3	$CO_{\_1}$	$CO_{\_2}$	$CO_{\_3}$	CO_T
Category	Run No	Load % Capacity	Startup Time.	Steady State Time	End Time	Startup CO emission	Steady State CO emission	End CO emission	Total CO emission
			min	min	min	g	g	g	g
I		< 15% of max							
II		16-24% of max							
III		25-50% of max							
IV		Max capacity							

Table 1D. Data Summary Part D

			E_1	E_2	E_3	$E_{1\_g/kg}$	$E_{2\_g/kg}$	$E_{3\_g/kg}$
Category	Run No	Load % Capacity	Startup PM	Steady State PM	End PM	Startup PM emission index	Steady State PM emission index	End PM emission index
			g	g	g	g/kg fuel	g/kg fuel	g/kg fuel
I		< 15% of max						
II		16-24% of max						
III		25-50% of max						
IV		Max capacity						

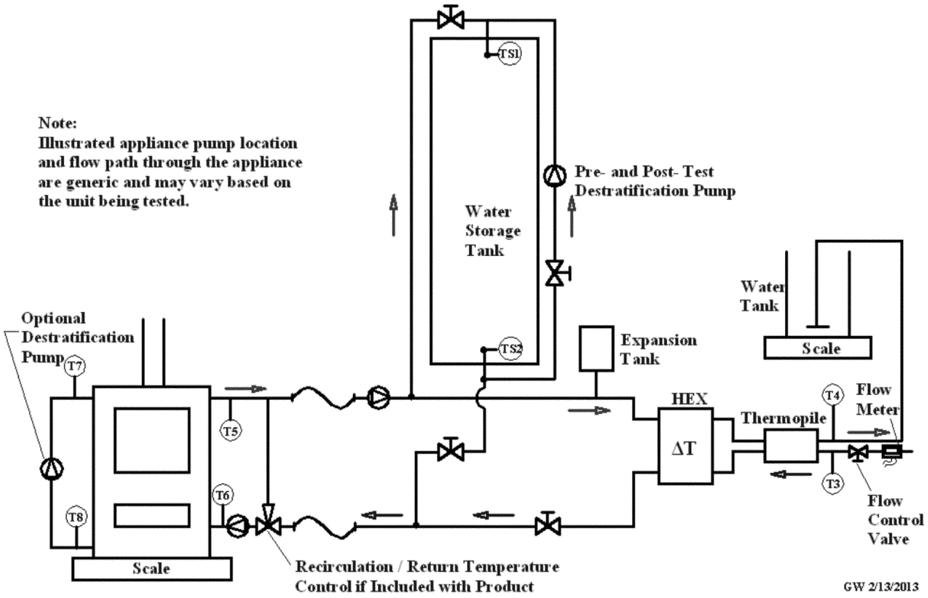
Table 1E: Label Summary Information

MANUFACTURER:			
MODEL NUMBER:			
ANNUAL EFFICIENCY RATING:	η_{avg}		**(Using higher heating value)**
PARTICLE EMISSIONS:	E_{avg}		grams/hr (Average)
			lbs/mmBtu/hr Output

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i}$ x F_i	$E_{g/MJ,i}$ x F_i	$E_{g/kg,i}$ x F_i	$E_{lb/mmBtu\ Out,i}$ x F_i	$E_{g/hr,i}$ x F_i
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Schematic of Equipment Test Setup



Note:
Illustrated appliance pump location and flow path through the appliance are generic and may vary based on the unit being tested.

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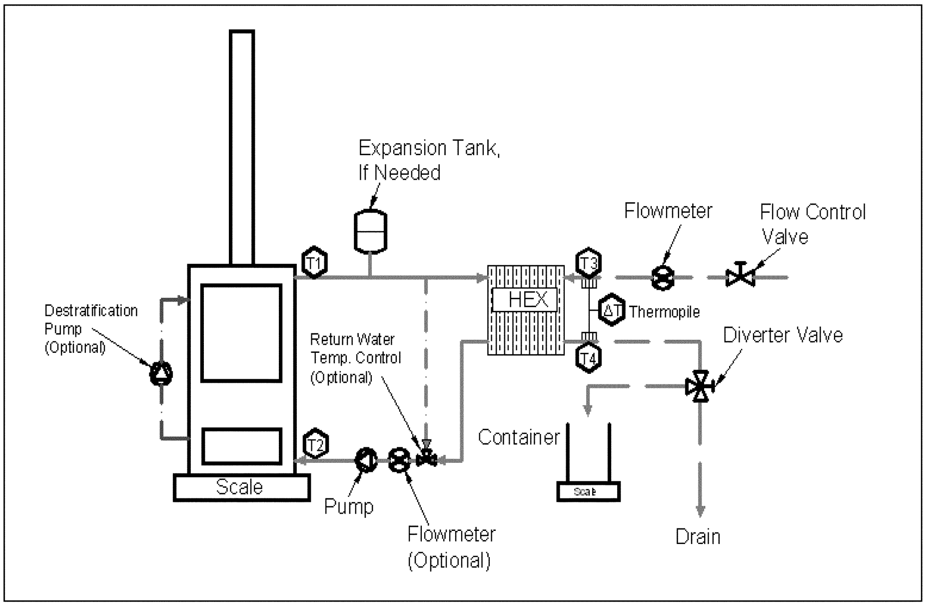
Figure 2. Schematic of Test Equipment Set-up



Note: Illustrated appliance pump location and flow path through the appliance.

METHOD 29—DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

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 have a thorough knowledge of at least the following additional test methods: Method 5 and Method 12.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Cadmium (Cd)	7440–43–9
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Lead (Pb)	7439–92–1
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Selenium (Se)	7782–49–2
Silver (Ag)	7440–22–4
Thallium (Tl)	7440–28–0
Zinc (Zn)	7440–66–6

1.2 Applicability. This method is applicable to the determination of metals emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.2.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

2.0 Summary of Method

2.1 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy

(CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. If one so chooses, AAS may be used for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program. Similarly, inductively coupled plasma-mass spectroscopy (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

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.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Nitric Acid (HNO_3). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.2 Sulfuric Acid (H_2SO_4). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m^3 for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.3 Hydrochloric Acid (HC1). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.4 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.5 Hydrogen Peroxide (H_2O_2). Irritating to eyes, skin, nose, and lungs. 30% H_2O_2 is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.6 Potassium Permanganate ($KMnO_4$). Caustic, strong oxidizer. Avoid bodily contact with.

5.2.7 Potassium Persulfate. Strong oxidizer. Avoid bodily contact with. Keep containers well closed and in a cool place.

5.3 Reaction Pressure. Due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the acidic $KMnO_4$ absorbing solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70–72 hole drilled in the container cap and Teflon liner has been used.

6.0 Equipment and Supplies

6.1 Sampling. A schematic of the sampling train is shown in Figure 29–1. It has general similarities to the Method 5 train.

6.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, sections 6.1.1.1 and 6.1.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

6.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, sections 6.1 and 6.2, respectively.

6.1.3 Filter Holder. Glass, same as Method 5, section 6.1.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

6.1.4 Filter Heating System. Same as Method 5, section 6.1.1.6.

6.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first HNO_3/H_2O_2 impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second HNO_3/H_2O_2 impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both acidified $KMnO_4$) impingers are the same as the first impinger in Method 5. Place a temperature sensor capable of measuring to within 1 °C (2 °F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

6.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

6.2 Sample Recovery. Same as Method 5, sections 6.2.1 through 6.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

6.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

6.2.2 Sample Storage Containers. Use glass bottles (see section 8.1 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified $KMnO_4$—containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

6.2.3 Graduated Cylinder. Glass or equivalent.

6.2.4 Funnel. Glass or equivalent.

6.2.5 Labels. For identifying samples.

6.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

6.3.2 Graduated Cylinders. For preparation of reagents.

6.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

6.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

6.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

6.3.6 Filter Funnels. For holding filter paper.

6.3.7 Disposable Pasteur Pipets and Bulbs.

6.3.8 Volumetric Pipets.

6.3.9 Analytical Balance. Accurate to within 0.1 mg.

6.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

6.3.11 Hot Plates.

6.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

6.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Reference 2 in section 16.0. Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

6.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10 °C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Reference 2 in section 16.0. See note 2: section 11.1.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

6.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Reference 2 in section 16.0.

6.3.14 Inductively Coupled Plasma-Mass Spectrometer.

Same as EPA Method 6020 in Reference 2 in section 16.0.

7.0 Reagents and Standards

7.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.2 Sampling Reagents.

7.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 µg/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO_2) or sulfur trioxide (SO_3) shall be as described in section 7.1.1 of Method 5.

7.2.2 Water. To conform to ASTM Specification D1193–77 or 91, Type II (incorporated by reference—see § 60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

7.2.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.2.4 HCl, Concentrated. Baker Instra-analyzed or equivalent.

7.2.5 H_2O_2, 30 Percent (V/V).

7.2.6 $KMnO_4$.

7.2.7 H_2SO_4, Concentrated.

7.2.8 Silica Gel and Crushed Ice. Same as Method 5, sections 7.1.2 and 7.1.4, respectively.

7.3 Pretest Preparation of Sampling Reagents.

7.3.1 HNO_3/H_2O_2 Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.2 Acidic $KMnO_4$ Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper.

7.3.3 HNO_3, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO_3, Concentrated. Fisher ACS grade or equivalent.

7.4.2 Water. To conform to ASTM Specifications D1193, Type II.

7.4.3 HNO_3, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5 Sample Digestion and Analysis Reagents. The metals standards, except Hg, may also be made from solid chemicals as described in Reference 3 in section 16.0. Refer to References 1, 2, or 5 in section 16.0 for additional information on Hg standards. The 1000 µg/ml Hg stock solution standard may be made according to section 7.2.7 of Method 101A.

7.5.1 HCl, Concentrated.

7.5.2 HF, Concentrated.

7.5.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

7.5.4 HNO_3, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.5 HNO_3, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.6 Water. To conform to ASTM Specifications D1193, Type II.

7.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Reference 2 In section 16.0 for preparation.

7.5.8 Stannous Chloride. See Reference 2 in section 16.0 for preparation.

7.5.9 $KMnO_4$, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.10 H_2SO_4, Concentrated.

7.5.11 Potassium Persulfate, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.12 Nickel Nitrate, $Ni(N0_3)_2 6H_20$.

7.5.13 Lanthanum Oxide, La_20_3.

7.5.14 Hg Standard (AAS Grade), 1000 µg/ml.

7.5.15 Pb Standard (AAS Grade), 1000 µg/ml.

7.5.16 As Standard (AAS Grade), 1000 µg/ml.

7.5.17 Cd Standard (AAS Grade), 1000 µg/ml.

7.5.18 Cr Standard (AAS Grade), 1000 µg/ml.

7.5.19 Sb Standard (AAS Grade), 1000 µg/ml.

7.5.20 Ba Standard (AAS Grade), 1000 µg/ml.

7.5.21 Be Standard (AAS Grade), 1000 µg/ml.

7.5.22 Co Standard (AAS Grade), 1000 µg/ml.

7.5.23 Cu Standard (AAS Grade), 1000 µg/ml.

7.5.24 Mn Standard (AAS Grade), 1000 µg/ml.

7.5.25 Ni Standard (AAS Grade), 1000 µg/ml.

7.5.26 P Standard (AAS Grade), 1000 µg/ml.

7.5.27 Se Standard (AAS Grade), 1000 µg/ml.

7.5.28 Ag Standard (AAS Grade), 1000 µg/ml.

7.5.29 Tl Standard (AAS Grade), 1000 µg/ml.

7.5.30 Zn Standard (AAS Grade), 1000 µg/ml.

7.5.31 Al Standard (AAS Grade), 1000 µg/ml.

7.5.32 Fe Standard (AAS Grade), 1000 µg/ml.

7.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

7.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Co, Cu, Fe.
III	Al, Cr, Ni.
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP-MS, follow Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i).

7.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO_3. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

7.5.36 Matrix Modifiers.

7.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(N0_3)_2 \cdot 6H_20$ or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

7.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La_20_3 in 10 ml of concentrated $HN0_3$, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

7.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

8.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, section 8.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.1.2.

8.1.3 Preparation of Sampling Train.

8.1.3.1 Set up the sampling train as shown in Figure 29–1. Follow the same general procedures given in Method 5, section 8.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 7.3.1 of this method) in each of the second and third impingers as shown in Figure 29–1. Place 100 ml of the acidic $KMnO_4$ absorbing solution (Section 7.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29–1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

8.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

8.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29–1 are not required.

8.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic $KMnO_4$ from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic $KMnO_4$.

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, section 8.4.2 (Pretest Leak-Check), section 8.4.3 (Leak-Checks During the Sample Run), and section 8.4.4 (Post-Test Leak-Checks).

8.1.5 Sampling Train Operation. Follow the procedures given in Method 5, section 8.5. When sampling for Hg, use a procedure analogous to that described in section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5–3 of Method 5.

8.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

8.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon® tape to close these openings.

8.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

8.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29–2a and 29–2b):

8.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

8.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

8.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

8.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

8.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container. Perform the rinses as applicable and generally as described in Method 12, section 8.7.1. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

NOTE: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

8.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO_3/H_2O_2 Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, section 8.7.3.

NOTE: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

8.2.9 Container Nos. 5A (0.1 N HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution).

8.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO_3 and place this rinse in Container No. 5A.

8.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic $KMnO_4$ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified $KMnO_4$ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the *Precaution:* in section 7.3.2.

NOTE: Due to the potential reaction of $KMnO_4$ with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70–72 hole drilled in the container cap and Teflon liner has been used successfully.

8.2.9.3 Wash the two permanganate impingers with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the 8 N HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing *both permanganate impingers combined*. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container with the 200 ml of water. Mark the height of the fluid level on the outside of the container in order to determine if leakage occurs during transport.

8.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

8.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

8.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

8.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

8.2.14 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

8.2.15 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in section 8.2.9.2. Read the *Precaution*: in section 7.3.2 and read the note in section 8.2.9.2.

8.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

8.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

8.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29–3.

8.3.1 Container No. 1 (Sample Filter).

8.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in section 11.2.1 of Method 5.

8.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to room temperature, and combine with the acid digested probe rinse as required in section 8.3.3.

8.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in section 8.3.1.2 and then combine the digestate with the digested filter sample.

8.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3. Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in section 8.3.1.2. The resultant combined sample is referred to as ''*Sample Fraction 1*''. Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is ''*Analytical Fraction 1*''. Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as ''*Analytical Fraction 1B*''. Label the remaining 250-ml portion as ''*Analytical Fraction 1A*''. Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1–3). Measure and record the total volume of this sample to within 0.5 ml and label it ''*Sample Fraction 2*''. Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot ''*Analytical Fraction 2B*''. Label the remaining portion of Container No. 4 as ''*Sample Fraction 2A*''. Sample Fraction 2A defines the volume of Analytical Fraction 2A *prior* to digestion. All of Sample Fraction 2A is digested to produce ''*Analytical Fraction 2A*''. Analytical Fraction 2A defines the volume of Sample Fraction 2A *after* its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes total *heating* time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

NOTE: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be

Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized *vented* container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per section 8.3.1, 100 ml from Container No. 7 per section 8.3.2, and 100 ml from Container No. 8A per section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per section 11.1.1 and/or section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in section 8 of Methods 6010 and 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent, analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29–2 and in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in § 60.17(i), or in *Standard Methods for Water and Wastewater* Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference-see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within ±0.5g of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617–13 ''Standard Specification for Laboratory Weights and Precision Mass Standards'' (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617–13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29–3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO_3/H_2O_2 impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the $H_2SO_4/KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29–2. These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29–3 to determine which techniques and procedures to apply for each target metal. Use Table 29–3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to section 10.3 and follow the quality control procedures specified in section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using note no. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see note no. 1 at end of this section). The total amount of Hg in the aliquot shall be less than 1 μg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See note no. 2 at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the ''0.15 HNO_3 percent dilution of the original sample'' is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE NO. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29–1, select a 10 ml aliquot for digestion and analysis as described.

NOTE NO. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.)*; (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = Analytical detection limit, μg/ml.
B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
C = Stack sample gas volume, dsm^3.
C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, μg/ml.
C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (μg/ml).
C_s = Concentration of a metal in the stack gas, mg/dscm.
D = In-stack detection limit, μg/m^3.
F_a = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see section 8.3.4.)
F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, F_d = 5).
Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, μg.
Hg_{bh2} = Total mass of Hg collected in Sample Fraction 2, μg.

$Hg_{bh3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.

Hg_{bhb} = Blank correction value for mass of Hg detected in back-half field reagent blanks, µg.

Hg_{fh} = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), µg.

Hg_{fhb} = Blank correction value for mass of Hg detected in front-half field reagent blank, µg.

Hg_t = Total mass of Hg collected in the sampling train, µg.

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), µg.

M_{bhb} = Blank correction value for mass of metal detected in back-half field reagent blank, µg.

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.

M_{fhb} = Blank correction value for mass of metal detected in front-half field reagent blank, µg.

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_t = Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the H_g calculation).

Q_{bh2} = Quantity of Hg, µg, TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis .

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh2}.

$Q_{bh3(A,B,C)}$ = Quantity of Hg, µg, *TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis* (see notes in sections 12.7.1 and 12.7.2 describing the quantity ''Q'' and calculate similarly).

Q_{fh} = Quantity of Hg, µg, *TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis.*

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see section 8.3.4.1 or 8.3.4.2, as applicable).

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml.

NOTE: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to section 11.1.3 and analyzed, V_{f1B} would be 0.02 ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml.

NOTE: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed, V_{f2B} would be 0.5 ml.

$V_{f3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in sections 12.7.1 and 12.7.2, describing the quantity ''V'' and calculate similarly).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4 = 10^{-3}$ mg/µg.

12.2 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in section 12.3 of Method 5.

12.3 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29–4 using the conditions described in section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \qquad \text{Eq. 29-1}$$

12.6 Metals (Except Hg) in Source Sample.

12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{al} F_d V_{soln,1} \qquad \text{Eq. 29-2}$$

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29–2 through 29–4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-3}$$

12.6.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = \left(M_{fh} - M_{fhb}\right) + \left(M_{bh} - M_{bhb}\right) \qquad \text{Eq. 29-4}$$

NOTE: If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to ''A'' µg (where ''A'' µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in in.^{2} of the sample filter), use M_{fhb} to correct the emission sample value (M_{fh}); if M_{fhb} exceeds ''A'' µg, use the greater of I or II:

I. ''A'' µg.

II. The lesser of (a) M_{fhb}, or (b) 5 percent of M_{fh}. If the measured blank value for the back-half (M_{bhb}) is in the range 0.0 to 1 µg, use M_{bhb} to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, use the greater of I or II:

I. 1 µg.

II. The lesser of (a) M_{bhb}, or (b) 5 percent of M_{bh}.

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount ofHg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29–5:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}}\left(V_{soln,1}\right) \qquad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29–6:

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}}\left(V_{soln,2}\right) \qquad \text{Eq. 29-6}$$

12.7.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29–7:

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}}\left(V_{soln,3(A,B,C)}\right) \qquad \text{Eq. 29-7}$$

12.7.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29–8:

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 29-8}$$

12.7.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29–9:

$$Hg_t = \left(Hg_{fh} - Hg_{fhb}\right) + \left(Hg_{bh} - Hg_{bhb}\right) \qquad \text{Eq. 29-9}$$

NOTE: If the total of the measured blank values (Hg_{fhb} + Hg_{bhb}) is in the range of 0.0 to 0.6 µg, then use the total to correct the sample value (Hg_{fh} + Hg_{bh}); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.

II. The lesser of (a) (Hg_{fhb} + Hg_{bhb}), or (b) 5 percent of the sample value (Hg_{fh} + Hg_{bh}).

12.8 Individual Metal Concentrations in Stack Gas. Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29–10:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \qquad \text{Eq. 29-10}$$

12.9 Isokinetic Variation and Acceptable Results. Same as Method 5, sections 12.11 and 12.12, respectively.

13.0 Method Performance

13.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml (μg/ml) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 μg/ml As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of Cd should be diluted to that level before analysis.

13.2 Analytical Detection Limits.

NOTE: See section 13.3 for the description of in-stack detection limits.

13.2.1 ICAP analytical detection limits for the sample solutions (based on *SW–846*, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP-MS analytical detection limits (based on *SW–846*, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

13.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on *SW–846*, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

13.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the *digestion* of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used. 13.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

13.3 In-stack Detection Limits.

13.3.1 For test planning purposes in-stack detection limits can be developed by using the following information: (1) The procedures described in this method, (2) the analytical detection limits described in section 13.2 and in *SW–846*,(3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29–1 and were calculated by using Eq. 29–1 shown in section 12.5.

13.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

13.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29–1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of *Hg only*, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

13.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29–1.

13.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

13.3.3.3 When both of the modifications described in sections 13.3.3.1 and 13.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

13.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at a sewage sludge incinerator were found to be as follows:

Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzer. Samples may also be analyzed by cold vapor atomic fluorescence spectrometry.

16.2 [Reserved]

17.0 References

1. Method 303F in *Standard Methods for the Examination of Water Wastewater*, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW–846, Third Edition, November 1986, with updates I, II, IIA, IIB and III. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, DC 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 29–1—In Stack Method Detection Limits (ug/m^3) for the Front-Half, the Back Half, and the Total Sampling Train Using ICAP, GFAAS, and CVAAS

Metal	Front-half: probe and filter	Back-half: impinters 1–3	Back-half: impringers 4–6 [a]	Total train
Antimony	[1]7.7 (0.7)	[1]3.8 (0.4)		[1]11.5 (1.1)
Arsenic	[1]12.7 (0.3)	[1]6.4 (0.1)		[1]19.1 (0.4)
Barium	0.5	0.3		0.8
Beryllium	[1]0.07 (0.05)	[1]0.04 (0.03)		[1]0.11 (0.08)
Cadmium	[1]1.0 (0.02)	[1]0.5 (0.01)		[1]1.5 (0.03)
Chromium	[1]1.7 (0.2)	[1]0.8 (0.1)		[1]2.5 (0.3)
Cobalt	[1]1.7 (0.2)	[1]0.8 (0.1)		[1]2.5 (0.3)
Copper	1.4	0.7		2.1
Lead	[1]10.1 (0.2)	[1]5.0 (0.1)		[1]15.1 (0.3)
Manganese	[1]0.5 (0.2)	[1]0.2 (0.1)		[1]0.7 (0.3)
Mercury	[2]0.06	[2]0.3	[2]0.2	[2]0.56
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	[1]18 (0.5)	[1]9 (0.3)		[1]27 (0.8)
Silver	1.7	0.9 (0.7)		2.6
Thallium	[1]9.6 (0.2)	[1]4.8 (0.1)		[1]14.4 (0.3)
Zinc	0.5	0.3		0.8

[a] Mercury analysis only.

[1] Detection limit when analyzed by ICAP or GFAAS as shown in parentheses (see section 11.1.2).

[2] Detection limit when anaylzed by CVAAS, estimated for Back-half and Total Train. See sections 13.2 and 11.1.3. Note: Actual method in-stack detection limits may vary from these values, as described in section 13.3.3.

TABLE 29–2—RECOMMENDED WAVELENGTHS FOR ICAP ANALYSIS

Analyte	Wavelength (nm)
Aluminum (Al)	308.215
Antimony (Sb)	206.833
Arsenic (As)	193.696
Barium (Ba)	455.403
Beryllium (Be)	313.042
Cadmium (Cd)	226.502
Chromium (Cr)	267.716
Cobalt (Co)	228.616
Copper (Cu)	328.754
Iron (Fe)	259.940
Lead (Pb)	220.353
Manganese (Mn)	257.610
Nickel (Ni)	231.604
Phosphorus (P)	214.914
Selenium (Se)	196.026
Silver (Ag)	328.068
Thallium (T$_1$)	190,864
Zinc (Zn)	213,856

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination.
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required.
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 μl of phosphorus acid to 1 ml of prepared sample in sampler cup.
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required.
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr.	Background correction required. Matrix matching or nitrous-oxide/acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization.
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful.
Ag	Aspiration	7760	328.1	Adsorption & scatter AgCl insoluble.	Background correction is required. Avoid hydrochloric acid unless silver is in solution as a chloride complex. Sample and standards monitored for aspiration rate.
Tl	Aspiration	7840	276.8		Background correction is required. Hydrochloric acid should not be used.
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride.	Background correction is required. Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination.	Strontium removes Cu and phosphate. Great care taken to avoid contamination.
Sb	Aspiration	7040	217.6	1000 mg/ml Pb, Ni, Cu, or acid.	Use secondary wavelength of 231.1 nm; match sample & standards acid concentration or use nitrous oxide/acetylene flame.
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction.
As	Furnace	7060	193.7	Arsenic Volatilization Aluminum.	Spike samples and add nickel nitrate solution to digestates prior to analysis. Use Zeeman background correction.
Ba	Aspiration	7080	553.6		
				Calcium.	
				Barium Ionization	High hollow cathode current and narrow band set. 2 ml of KCl per 100 m1 of sample.
Be	Aspiration	7090	234.9	500 ppm Al. High Mg and Si.	Add 0.1% fluoride.
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects.
Cd	Aspiration	7130	228.8	Absorption and light scattering.	Background correction is required.

TABLE 29–3—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCES FOR AAS ANALYSIS—Continued

Metal	Technique	SW–846 [1] Methods No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Cd	Furnace	7131	228.8	As above	As above.
				Excess Chloride	Ammonium phosphate used as a matrix modifier.
				Pipet Tips	Use cadmium-free tips.
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards—Consult mfgs' literature.
Co	Furnace	7201	240.7	Excess chloride	Use Method of Standard Additions.
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a know constant effect and to eliminate effect of phosphate.
Cu	Aspiration	7210	324.7	Absorption and Scatter	Consult manufacturer's manual.

[1] Refer to EPA publication SW–846 (Reference 2 in section 16.0).

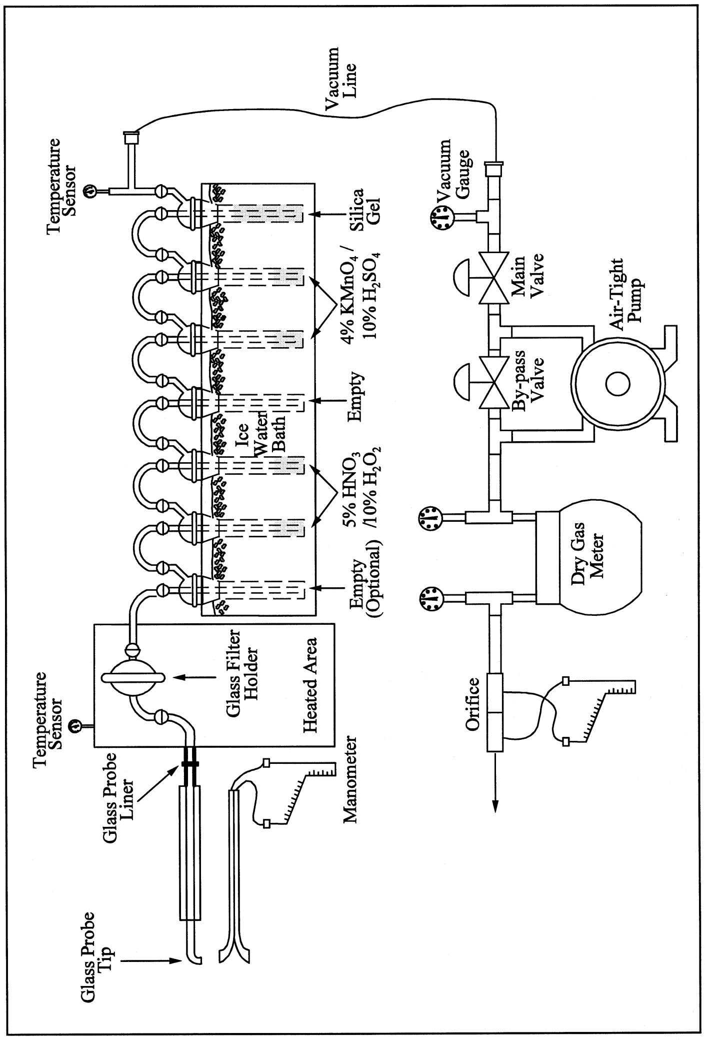
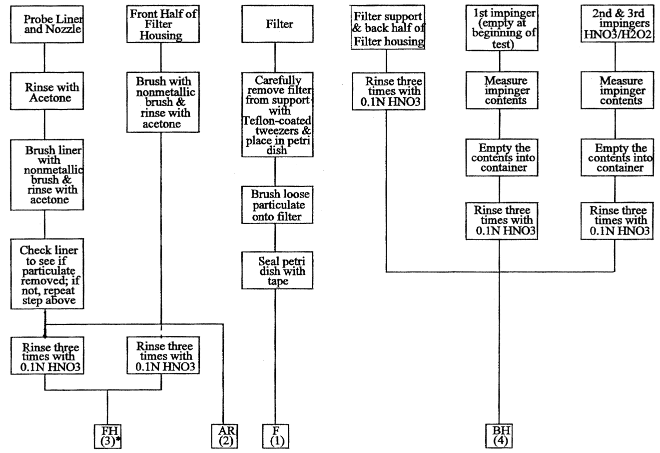


Figure 29-1. Sampling Train.



* Number in parentheses indicated container number

Figure 29-2a. Sample Recovery Scheme.

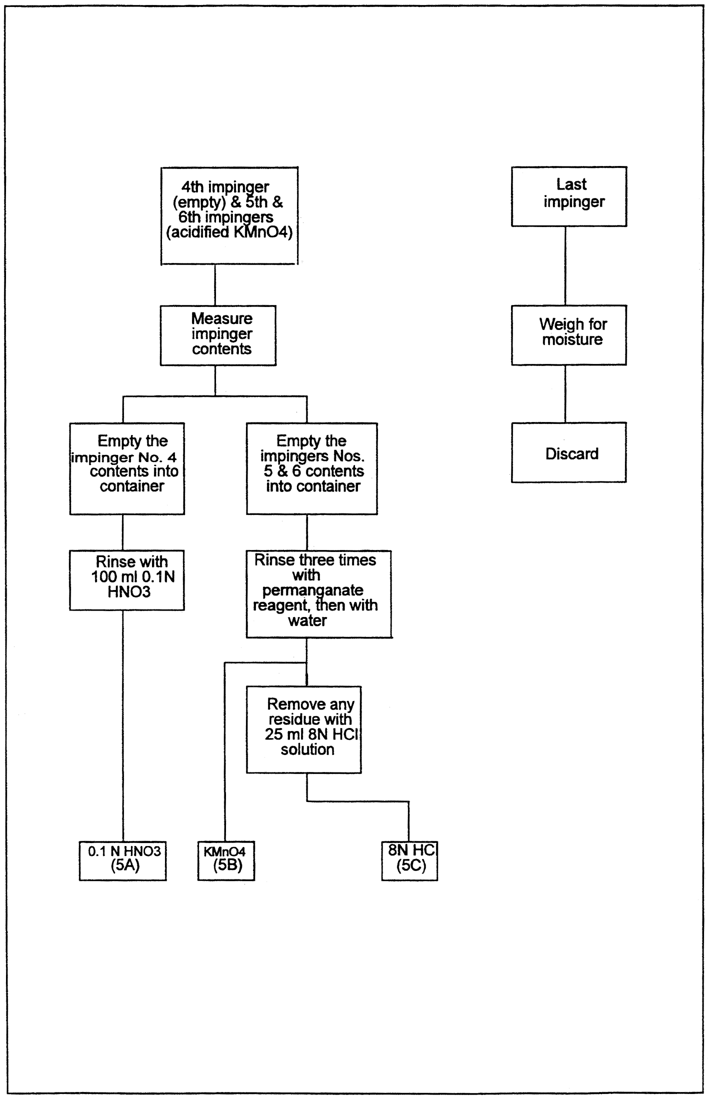


Figure 29-2b. Sample Recovery Scheme.

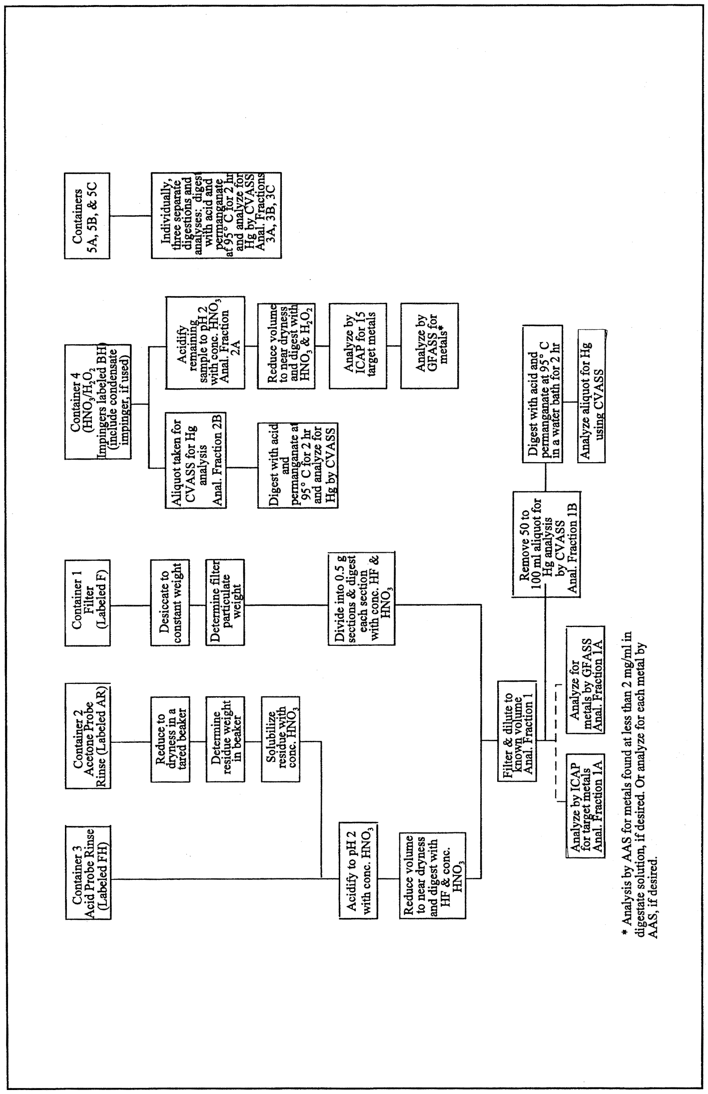


Figure 29-3. Sample Preparation and Analysis Scheme.

METHOD 30A—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1.0 Scope and Application

What Is Method 30A?

Method 30A is a procedure for measuring total vapor phase mercury (Hg) emissions from stationary sources using an instrumental analyzer. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury continuous emissions monitoring systems (Hg CEMS) and sorbent trap monitoring systems at coal-fired combustion sources. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing site. This method does not completely describe all equipment, supplies, and sampling procedures and analytical procedures you will need but refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are also found in appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, which represents the sum of elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in mass concentration units of micrograms per cubic meter (μg/m^3).

Analyte	CAS No.	Sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically <2% of Calibration Span.
Oxidized Hg (Hg^{+2})		(Same).

1.2 Applicability. When is this method required? Method 30A is offered as a reference method for emission testing and for RATAs of Hg CEMS and sorbent trap monitoring systems at coal-fired boilers. Method 30A may also be specified for other source categories in the future, either by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIP), or operating permits that require measurement of Hg concentrations in stationary source emissions to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30A has been designed to provide data of high and known quality for Hg emission testing and for relative accuracy testing of Hg monitoring systems including Hg CEMS and sorbent trap monitoring systems. In these and other applications, the principle objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, calibration standards prepared according to an EPA traceability protocol must be used and measurement system performance tests are required.

2.0 Summary of Method

In this method, a sample of the effluent gas is continuously extracted and conveyed to an analyzer capable of measuring the total vapor phase Hg concentration. Elemental and oxidized mercury (i.e., Hg^0 and Hg^{+2}) may be measured separately or simultaneously but, for purposes of this method, total vapor phase Hg is the sum of Hg^0 and Hg^{+2}. You must meet the performance requirements of this method (i.e., system calibration, interference testing, dynamic spiking, and system integrity/drift checks) to validate your data. The dynamic spiking requirement is deferred until January 1, 2009.

3.0 Definitions

3.1 *Calibration Curve* means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

3.2 *Calibration Gas* means a gas standard containing Hg^0 or $HgCl_2$ at a known concentration that is produced and certified in accordance with an EPA traceability protocol for certification of Hg calibration standards.

3.2.1 *Zero Gas* means a calibration gas with a concentration that is below the level detectable by the measurement system.

3.2.2 *Low-Level Gas* means a calibration gas with a concentration that is 10 to 30 percent of the calibration span.

3.2.3 *Mid-Level Gas* means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

3.2.4 *High-Level Gas* means a calibration gas whose concentration is equal to the calibration span.

3.3 *Converter* means a device that reduces oxidized mercury (Hg^{+2}) to elemental mercury (Hg^0).

3.4 *Calibration Span* means the upper limit of valid instrument response during sampling. To the extent practicable the measured emissions are to be between 10 and 100 percent of the selected calibration span (*i.e.*, the measured emissions should be within the calibrated range determined by the Low- and High-Level gas standards). It is recommended that the calibration span be at least twice the native concentration to accommodate the dynamic spiking procedure.

3.5 *Centroidal Area* means the central area that has the same shape as the stack or duct cross section and is no greater than one percent of the stack or duct total cross-sectional area.

3.6 *Data Recorder* means the equipment that permanently records the concentrations reported by the analyzer.

3.7 *Drift Check* means the test to determine the difference between the measurement system readings obtained in a post-run system integrity check and the prior pre-run system integrity check at a specific calibration gas concentration level (*i.e.*, zero, mid-level, or high-level).

3.8 *Dynamic Spiking* means a procedure in which a known mass or concentration of vapor phase $HgCl_2$ is injected into the probe sample gas stream at a known flow rate, in order to assess the effects of the flue gas matrix on the accuracy of the measurement system.

3.9 *Gas Analyzer* means the equipment that detects the total vapor phase Hg being measured and generates an output proportional to its concentration.

3.10 *Interference Test* means the test to detect analyzer responses to compounds other than Hg, usually gases present in the measured gas stream, that are not adequately accounted for in the calibration procedure and may cause measurement bias.

3.11 *Measurement System* means all of the equipment used to determine the Hg concentration. The measurement system may generally include the following major subsystems: sample acquisition, Hg^{+2} to Hg^0 converter, sample transport, sample conditioning, flow control/gas manifold, gas analyzer, and data recorder.

3.12 *Native Concentration* means the total vapor phase Hg concentration in the effluent gas stream.

3.13 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.14 *Response Time* means the time it takes for the measurement system, while operating normally at its target sample flow rate or dilution ratio, to respond to a known step change in gas concentration (from a low-level to a high-level gas) and to read within 5 percent of the stable high-level gas response.

3.15 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.16 *System Calibration Error* means the difference between the measured concentration of a low-, mid-, or high-level Hg^0 calibration gas and the certified concentration of the gas when it is introduced in system calibration mode.

3.17 *System Calibration Mode* means introducing the calibration gases into the measurement system at the probe, upstream of all sample conditioning components.

3.18 *Test* refers to the series of runs required by the applicable regulation.

4.0 Interferences

Interferences will vary among instruments and potential instrument-specific spectral and matrix interferences must be evaluated through the interference test and the dynamic spiking tests.

5.0 Safety

What safety measures should I consider when using this method?

This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

6.0 Equipment and Supplies

6.1 What do I need for the measurement system? This method is intended to be applicable to multiple instrumental technologies. You may use any equipment and supplies that meet the following specifications.

6.1.1 All wetted sampling system components, including probe components prior to the point at which the calibration gas is introduced, must be chemically inert to all Hg species. Materials such as perfluoroalkoxy (PFA) Teflon™, quartz, treated stainless steel (SS) are examples of such materials. [NOTE: These materials of construction are required because components prior to the calibration gas injection point are not included in the system calibration error, system integrity, and interference tests.]

6.1.2 The interference, system calibration error, system integrity, drift and dynamic spiking test criteria must all be met by the system used.

6.1.3 The system must be capable of measuring and controlling sample flow rate.

6.1.4 All system components prior to the Hg^{+2} to Hg^0 converter must be maintained at a sample temperature above the acid gas dew point.

6.2 Measurement System Components. Figure 30A–1 in section 17.0 is an example schematic of a Method 30A measurement system.

6.2.1 Sample Probe. The probe must be made of the appropriate materials as noted in section 6.1.1, heated when necessary (see section 6.1.4), configured with ports for introduction of calibration and spiking gases, and of sufficient length to traverse all of the sample points.

6.2.2 Filter or Other Particulate Removal Device. The filter or other particulate removal device is considered to be a part of the measurement system, must be made of appropriate materials as noted in section 6.1.1, and must be included in all system tests.

6.2.3 Sample Line. The sample line that connects the probe to the converter, conditioning system and analyzer must be made of appropriate materials as noted in section 6.1.1.

6.2.4 Conditioning Equipment. For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe, or sample line to avoid condensation prior to the moisture removal component is also required. For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

6.2.5 Sampling Pump. A pump is needed to push or pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. If a mechanical sample pump is used and its surfaces are in contact with the sample gas prior to detection, the pump must be leak free and must be constructed of a material that is non-reactive to the gas being sampled (see section 6.1.1). For dilution-type measurement systems, an ejector pump (eductor) may be used to create a sufficient vacuum that sample gas will be drawn through a critical orifice at a constant rate. The ejector pump may be constructed of any material that is non-reactive to the gas being sampled.

6.2.6 Calibration Gas System(s). One or more systems may be needed to introduce calibration gases into the measurement system. A system should be able to flood the sampling probe sufficiently to prevent entry of gas from the effluent stream.

6.2.7 Dynamic Spiking Port. For the purposes of the dynamic spiking procedure described in section 8.2.7, the measurement system must be equipped with a port to allow introduction of the dynamic spike gas stream with the sample gas stream, at a point as close as possible to the inlet of the probe so as to ensure adequate mixing. The same port used for system calibrations and calibration error checks may be used for dynamic spiking purposes.

6.2.8 Sample Gas Delivery. The sample line may feed directly to a converter, to a bypass valve (for speciating systems), or to a sample manifold. All valve and/or manifold components must be made of material that is non-reactive to the gas sampled and the calibration gas, and must be configured to safely discharge any excess gas.

6.2.9 Hg Analyzer. An instrument is required that continuously measures the total vapor phase Hg in the gas stream and meets the applicable specifications in section 13.0.

6.2.10 Data Recorder. A recorder, such as a computerized data acquisition and handling system (DAHS), digital recorder, strip chart, or data logger, is required for recording measurement data.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.5), either Method 4 in appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Calibration Gases. What calibration gases do I need? You will need calibration gases of known concentrations of Hg^0 and $HgCl_2$. Special reagents and equipment may be required to prepare the $HgCl^2$ gas standards (e.g., a NIST-traceable solution of $HgCl_2$ and a gas generator equipped with mass flow controllers).

The following calibration gas concentrations are required:

7.1.1 High-Level Gas. Equal to the selected calibration span.

7.1.2 Mid-Level Gas. 40 to 60 percent of the calibration span.

7.1.3 Low-Level Gas. 10 to 30 percent of the calibration span.

7.1.4 Zero Gas. No detectable Hg.

7.1.5 Dynamic Spike Gas. The exact concentration of the $HgCl_2$ calibration gas used to perform the pre-test dynamic spiking procedure described in section 8.2.7 depends on the native Hg concentration in the stack The spike gas must produce a spiked sample concentration above the native concentration, as specified in section 8.2.7.2.2.

7.2 Interference Test. What reagents do I need for the interference test? Use the appropriate test gases listed in Table 30A–3 in section 17.0 (i.e., the potential interferents for the source to be tested, as identified by the instrument manufacturer) to conduct the interference check. These gases need not be of protocol gas quality.

8.0 Sample Collection

Emission Test Procedure

Figure 30A–2 in section 17.0 presents an overview of the test procedures required by this method. Since you may choose different options to comply with certain performance criteria, you must identify the specific options and associated frequencies you select and document your results in regard to the performance criteria.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select?

8.1.1 When this method is used solely for Hg emission testing (e.g., to determine compliance with an emission standard or limit), use twelve sampling points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, you may conduct a stratification test as described in section 8.1.3 to determine the number and location of the sampling points.

8.1.2 When this method is used for relative accuracy testing of a Hg CEMS or sorbent trap monitoring system, follow the sampling site selection and sampling point layout procedures for gas monitor RATA testing described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2, section 8.1.3 of appendix B to this part or section 6.5.6 of appendix A to part 75 of this chapter), with one exception. If you elect to perform stratification testing as part of the sampling point selection process, perform the testing in accordance with section 8.1.3 of this method (see also ''Summary Table of QA/QC Requirements'' in section 9.0).

8.1.3 Determination of Stratification. If you elect to perform stratification testing as part of the sampling point selection process and the test results show your effluent gas stream to be unstratified or minimally stratified, you may be allowed to sample at fewer points or at different points than would otherwise be required.

8.1.3.1 Test Procedure. To test for stratification, use a probe of appropriate length to measure the total vapor phase Hg concentration at twelve traverse points located according to Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part. Alternatively, for a sampling location where stratification is expected (e.g., after a wet scrubber or at a point where dissimilar gas streams are combined together), if a 12-point Hg stratification test has been previously performed at that location and the results of the test showed the location to be minimally stratified or unstratified according to the criteria in section 8.1.3.2, you may perform an abbreviated 3-point or 6-point Hg stratification test at the points specified in section 6.5.6.2(a) of appendix A to part 75 of this chapter in lieu of performing the 12-point test. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean Hg concentrations.

8.1.3.2 Acceptance Criteria and Sampling Point Location.

8.1.3.2.1 If the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a) ±5 percent of the mean concentration; or (b) ±0.2 μg/m^3 (whichever is less restrictive), the gas stream is considered to be unstratified and you may collect samples from a single point that most closely matches the mean.

8.1.3.2.2 If the 5 percent or 0.2 μg/m^3 criterion in section 8.1.3.2.1 is not met, but the Hg concentration at each traverse point differs from the mean concentration for all traverse points by no more than: (a)±10 percent of the mean; or (b)±0.5 μg/m^3 (whichever is less restrictive), the gas stream is considered to be minimally stratified, and you may take samples from three points, provided the points are located on the measurement line exhibiting the highest average Hg concentration during the stratification test. If the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), locate the three sampling points at 0.4, 1.0, and 2.0 meters from the stack or duct wall. Alternatively, if a RATA required by part 75 of this chapter is being conducted, you may locate the three points at 4.4, 14.6, and 29.6 percent of the duct diameter, in accordance with Method 1 in appendix A–1 to this part. For stack or duct diameters of 2.4 meters (7.8 ft) or less, locate the three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line.

8.1.3.2.3 If the gas stream is found to be stratified because the 10 percent or 0.5 μg/m^3 criterion in section 8.1.3.2.2 is not met, then either locate three sampling points at 16.7, 50.0, and 83.3 percent of the measurement line that exhibited the highest average Hg concentration during the stratification test, or locate twelve traverse points for the test in accordance with Table 1–1 or Table 1–2 of Method 1 in appendix A–1 to this part; or, if a RATA required by part 75 of this chapter is being conducted, locate six Method 1 points along the measurement line that exhibited the highest average Hg concentration.

8.1.3.3 Temporal Variations. Temporal variations in the source Hg concentration during a stratification test may complicate the determination of stratification. If temporal variations are a concern, you may use the following procedure to normalize the stratification test data. A second Hg measurement system, i.e., either an installed Hg CEMS or another Method 30A system, is required to perform this procedure. Position the sampling probe of the second Hg measurement system at a fixed point in the stack or duct, at least one meter from the stack or duct wall. Then, each time that the Hg concentration is measured at one of the stratification test points, make a concurrent measurement of Hg concentration at the fixed point. Normalize the Hg concentration measured at each traverse point, by multiplying it by the ratio of $C_{F,avg}$ to C_F, where C_F is the corresponding fixed-point Hg concentration measurement, and $C_{F,avg}$ is the average of all of the fixed-point measurements over the duration of the stratification test. Evaluate the results of the stratification test according to section 8.1.3.2, using the normalized Hg concentrations.

8.1.3.4 Stratification Testing Exemption. Stratification testing need not be performed at a test location where it would otherwise be required to justify using fewer sample points or different sample points, if the owner or operator documents that the Hg concentration in the stack gas is expected to be 3 μg/m^3 or less at the time of a Hg monitoring system RATA or an Hg emissions test. To demonstrate that a particular test location qualifies for the stratification testing exemption, representative Hg emissions data must be collected just prior to the RATA or emissions test. At least one hour of Hg concentration data is required for the demonstration. The data used for the demonstration shall be recorded at process operating conditions that closely approximate the operating conditions that will exist during the RATA or emissions test. It is recommended that collection of the demonstration data be integrated with the on-site pretest procedures required by the reference method being used for the RATA or emissions test (whether this method or another approved Hg reference method is used). Quality-assured data from an installed Hg monitoring system may also be used for the demonstration. If a particular test location qualifies for the stratification testing exemption, sampling shall be performed at three points, as described in section 8.1.3.2.2 of this method. The owner or operator shall fully document the method used to collect the demonstration data and shall keep this documentation on file with the data from the associated RATA or Hg emissions test.

8.1.3.5 Interim Alternative Stratification Test Procedures. In the time period between the effective date of this method and January 1, 2009, you may follow one of the following two procedures. Substitute a stratification test for sulfur dioxide (SO_2) for the Hg stratification test described in section 8.1.3.1. If this option is chosen, follow the test procedures in section 6.5.6.1 of appendix A to part 75 of this chapter. Evaluate the test results and determine the sampling point locations according to section 6.5.6.3 of appendix A to part 75 of this chapter. If the sampling location is found to be minimally stratified or unstratified for SO_2, it shall be considered minimally stratified or unstratified for Hg. Alternatively, you may forgo stratification testing, assume the gas stream is minimally stratified, and sample at three points as described in section 8.1.3.2.2 of this method.

8.2 Initial Measurement System Performance Tests. What initial performance criteria must my system meet before I begin sampling? Before measuring emissions, perform the following procedures:

(a) Interference Test;

(b) Calibration Gas Verification;

(c) Measurement System Preparation;

(d) 3-Point System Calibration Error Test;

(e) System Integrity Check;

(f) Measurement System Response Time Test; and

(g) Dynamic Spiking Test.

8.2.1 Interference Test (Optional). Your measurement system should be free of known interferences. It is recommended that you conduct this interference test of your measurement system prior to its initial use in the field to verify that the candidate test instrument is free from inherent biases or interferences resulting from common combustion emission constituents. If you have multiple measurement systems with components of the same make and model numbers, you need only perform this interference check on one system and you may also rely on an interference test conducted by the manufacturer on a system having components of the same make and model(s) of the system that you use. The interference test procedure is found in section 8.6 of this method.

8.2.2 Calibration Gas Verification. How must I verify the concentrations of my calibration gases?

8.2.2.1 Cylinder Gas Standards. When cylinder gas standards are used for Hg^0, obtain a certificate from the gas manufacturer and confirm that the documentation includes all information required by an EPA traceability protocol (see section 16). Confirm that the manufacturer certification is complete and current. Ensure that the calibration gas certifications have not expired.

8.2.2.2 Other Calibration Standards. All other calibration standards for $HgCl_2$ and Hg^0, such as gas generators, must meet the requirements of an EPA traceability protocol (see section 16), and the certification procedures must be fully documented in the test report.

8.2.2.3 Calibration Span. Select the calibration span (i.e., high-level gas concentration) so that the measured source emissions are 10 to 100 percent of the calibration span. This requirement is waived for applications in which the Hg concentrations are consistently below 1 μg/m³; however, the calibration span for these low-concentration applications shall not exceed 5 μg/m³.

8.2.3 Measurement System Preparation. How do I prepare my measurement system for use? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable). Then, conduct a 3-point system calibration error test using Hg^0 as described in section 8.2.4, an initial system integrity check using $HgCl_2$ and a zero gas as described in section 8.2.5, and a pre-test dynamic spiking test as described in section 8.2.7.

8.2.4 System Calibration Error Test. Conduct a 3-point system calibration error test before the first test run. Use Hg^0 standards for this test. Introduce the low-, mid-, and high-level calibration gases in any order, in system calibration mode, unless you desire to determine the system response time during this test, in which case, inject the gases such that the high-level injection directly follows the low-level injection. For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and you may make only the adjustments necessary to maintain the proper ratio. After each gas injection, wait until a stable response has been obtained. Record the analyzer's final, stable response to each calibration gas on a form similar to Table 30A–1 in section 17.0. For each calibration gas, calculate the system calibration error using Equation 30A–1 in section 12.2. The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met for all three gases, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.2.5 System Integrity Check. Perform a two-point system integrity check before the first test run. Use the zero gas and either the mid- or high-level $HgCl_2$ calibration gas for the check, whichever one best represents the total vapor phase Hg concentration levels in the stack. Record the data on a form similar to Table 30A–2 in section 17.0. The system integrity check specification in section 13.2 must be met for both the zero gas and the mid- or high-level gas. If the system integrity specification is not met for both gases, take corrective action and repeat the test until an acceptable system integrity check is achieved.

8.2.6 Measurement System Response Time. The measurement system response time is used to determine the minimum sampling time for each sampling point and is equal to the time that is required for the measured Hg concentration to increase from the stable low-level calibration gas response to a value within 5 percent of the stable high-level calibration gas response during the system calibration error test in section 8.2.4. Round off the measured system response time to the nearest minute.

8.2.7 Dynamic Spiking Test. You must perform dynamic spiking prior to the first test run to validate your test data. The purpose of this procedure is to demonstrate that the site-specific flue gas matrix does not adversely affect the accuracy of the measurement system. The specifications in section 13.5 must be met to validate your data. If these specifications are not met for the pretest dynamic spiking, you may not proceed with the test until satisfactory results are obtained. For the time period between the effective date of this method and January 1, 2009, the dynamic spiking requirement is waived.

8.2.7.1 How do I perform dynamic spiking? Dynamic spiking is a gas phase application of the method of standard additions, which involves injecting a known quantity of Hg into the measurement system upstream of all sample conditioning components, similar to system calibration mode, except the probe is not flooded and the resulting sample stream includes both effluent gas and the spike gas. You must follow a written procedure that details how the spike is added to the system, how the spike dilution factor (DF) is measured, and how the Hg concentration data are collected and processed.

8.2.7.2 Spiking Procedure Requirements.

8.2.7.2.1 Spiking Gas Requirements. The spike gas must also be a $HgCl_2$ calibration gas certified by an EPA traceability protocol. You must choose concentrations that can produce the target levels while being injected at a volumetric flow rate that is ≤ 20 percent of the total volumetric flow rate through the measurement system (i.e., sample flow rate plus spike gas flow rate).

8.2.7.2.2 Target Spiking Level. The target level for spiking must be 150 to 200 percent of the native Hg concentration; however, if the native Hg concentration is <1 $\mu g/m^3$, set the target level to add between 1 and 4 $\mu g/m^3$ Hg^{+2} to the native concentration. Use Equation 30A–5 in section 12.5 to calculate the acceptable range of spike gas concentrations at the target level. Then select a spike gas concentration in that range.

8.2.7.2.3 Spike Injections. You must inject spikes in such a manner that the spiking does not alter the total volumetric sample system flow rate and dilution ratio (if applicable). You must collect at least 3 data points, and the relative standard deviation (RSD) specification in section 13.5 must be met. Each data point represents a single spike injection, and pre- and post-injection measurements of the native Hg concentration (or diluted native concentration, as applicable) are required for each spike injection.

8.2.7.2.4 Spike Dilution Factor (DF). For each spike injection, DF, the dilution factor must be determined. DF is the ratio of the total volumetric flow rate of gas through the measurement system to the spike gas flow rate. This factor must be ≥ 5. The spiking mass balance calculation is directly dependent on the accuracy of the DF determination. As a result, high accuracy total volumetric flow rate and spike gas flowrate measurements are required. These flow rates may be determined by direct or indirect measurement. Calibrated flow meters, venturies, orifices or tracer gas measurements are examples of potential flow measurement techniques.

8.2.7.2.5 Concentrations. The measurement system must record total vapor phase Hg concentrations continuously during the dynamic spiking procedure. It is possible that dynamic spiking at a level close to 200 percent of the native Hg concentration may cause the measured Hg concentration to exceed the calibration span value. Avoid this by choosing a lower spiking level or by recalibration at a higher span. The measurements shall not exceed 120 percent of the calibration span. The "baseline" measurements made between spikes may represent the native Hg concentration (if spike gas flow is stopped between injections) or the native Hg concentration diluted by blank or carrier gas flowing at the same rate as the spike gas (if gas flow cannot be stopped between injections). Each baseline measurement must include at least 4 readings or 1 minute (whichever is greater) of stable responses. Use Equation 30A–10 or 30A–11 in section 12.10 (as applicable) to convert baseline measurements to native concentration.

8.2.7.2.6 Recovery. Calculate spike recoveries using Equation 30A–7 in section 12.7. Mass recoveries may be calculated from stable responses based on injected mass flows or from integrated response peaks based on total mass injected. Calculate the mean and RSD for the three (or more) spike injections and compare to the specifications in section 13.5.

8.2.7.2.7 Error Adjustment Option. You may adjust the measurement data collected during dynamic spiking for the system calibration error using Equation 30A–3 in section 12. To do this, perform the initial system integrity check prior to the dynamic spiking test, and perform another system integrity check following the dynamic spiking test and before the first test run. If you choose this option, you must apply Equation 30A–3 to both the spiked sample concentration measurement (C_{ss}) and the baseline or native concentration measurement (C_{native}), each substituted in place of C_{avg} in the equation.

8.2.7.3 Example Spiking Procedure Using a Hot Vapor Calibration Source Generator.

(a) Introduce the spike gas into the probe using a hot vapor calibration source generator and a solution of $HgCl_2$ in dilute HC1 and HNO_3. The calibrator uses a mass flow controller (accurate within 2 percent) to measure the gas flow, and the solution feed is measured using a top-loading balance accurate to 0.01g. The challenges of injecting oxidized Hg may make it impractical to stop the flow of gas between spike injections. In this case, operate the hot vapor calibration source generator continuously during the spiking procedure, swapping blank solutions for $HgCl_2$ solutions when switching between spiking and baseline measurements.

(b) If applicable, monitor the measurement system to make sure the total sampling system flow rate and the sample dilution ratio do not change during this procedure. Record all data on a data sheet similar to Table 30A–5 in section 17.0. If the Hg measurement system design makes it impractical to measure the total volumetric flow rate through the system, use a spike gas that includes a tracer for measuring the dilution factor, DF (see Equation 30A–9 in section 12.9). Allow the measurements to stabilize between each spike injection, average the pre- and post-injection baseline measurements, and calculate the native concentration. If this measurement shifts by more than 5 percent during any injection, it may be necessary to discard that data point and repeat the injection to achieve the required RSD among the injections. If the spikes persistently show poor repeatability, or if the recoveries are not within the range specified in section 13.5, take corrective action.

8.2.8 Run Validation. How do I confirm that each run I conduct is valid?

8.2.8.1 System Integrity Checks.

(a) Before and after each test run, perform a two-point system integrity check using the same procedure as the initial system integrity check described in section 8.2.5. You may use data from that initial system integrity check as the pre-run data for the first test run, provided it is the most recent system integrity check done before the first run. You may also use the results of a successful post-run system integrity check as the pre-run data for the next test run. Do not make any adjustments to the measurement system during these checks, other than to maintain the target calibration gas flow rate and the proper dilution ratio.

(b) As a time-saving alternative, you may, at the risk of invalidating multiple test runs, skip one or more integrity checks during a test day. Provided there have been no auto-calibrations or other instrument alterations, a single integrity check may suffice as a post-run check to validate (or invalidate) as many consecutive test runs as can be completed during a single test day. All subsequent test days must begin with a pre-run system integrity check subject to the same performance criteria and corrective action requirements as a post-run system integrity check.

(c) Each system integrity check must meet the criteria for system integrity checks in section 13.2. If a post-run system integrity check is failed, all test runs since the last passed system integrity check are invalid. If a post-run or a pre-run system integrity check is failed, you must take corrective action and pass another 3-point Hg^0 system calibration error test (Section 8.2.4) followed by another system integrity check before conducting any additional test runs. Record the results of the pre- and post-run system integrity checks on a form similar to Table 30A–2 in section 17.0.

8.2.8.2 Drift Check. Using the data from the successful pre- and post-run system integrity checks, calculate the zero and upscale drift, using Equation 30A–2 in section 12.3. Exceeding the section 13.3 specification does not invalidate the run, but corrective action must be taken and a new 3-point Hg^0 system calibration error test and a system integrity check must be passed before any more runs are made.

8.3 Dilution-Type Systems—Special Considerations. When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate dilution controller must be used to maintain the correct dilution ratio during sampling. The dilution controller should be capable of monitoring the dilution air pressure, orifice upstream pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures, dilution air, and the stack gas molecular weight must be considered because these can affect the dilution ratio and introduce measurement bias.

8.4 Sampling.

(a) Position the probe at the first sampling point. Allow the system to flush and equilibrate for at least two times the measurement system response time before recording any data. Then, traverse and record measurements at all required sampling points. Sample at each traverse point for an equal length of time, maintaining the appropriate sample flow rate or dilution ratio (as applicable). For all Hg instrumental method systems, the minimum sampling time at each sampling point must be at least two times the system response time, but not less than 10 minutes. For concentrating systems, the minimum sampling time must also include at least 4 concentration measurement cycles.

(b) After recording data for the appropriate period of time at the first traverse point, you may move the sample probe to the next point and continue recording, omitting the requirement to allow the system to equilibrate for two times the system response time before recording data at the subsequent traverse points. You must, however, sample at this and all subsequent traverse points for the required minimum amount of time specified in this section. If you must remove the probe from the stack for any reason, you must again allow the sampling system to equilibrate for at least two times the system response time prior to resuming data recording.

(c) If at any point the measured Hg concentration exceeds the calibration span value, you must at a minimum identify and report this as a deviation from the method. Depending on the data quality objectives of the test, this event may require corrective action before proceeding. If the average Hg concentration for any run exceeds the calibration span value, the run is invalidated.

8.5 Moisture Correction. If the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emission limit; or (2) a Hg CEMS or sorbent trap monitoring system being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 in appendix A–3 of this part or other appropriate methods, subject to the approval of the Administrator.

8.6 Optional Interference Test Procedure.

(a) Select an appropriate calibration span that reflects the source(s) to be tested and perform the interference check at 40 percent of the lowest calibration span value anticipated, e.g., 10 $\mu g/m^3$. Alternatively, successfully conducting the interference test at an absolute Hg concentration of 2 $\mu g/m^3$ will demonstrate performance for an equivalent calibration span of 5 $\mu g/m^3$, the lowest calibration span allowed for Method 30A testing. Therefore, performing the interference test at the 2 μ/m^3 level will serve to demonstrate acceptable performance for all calibration spans greater than or equal to 5 $\mu g/m^3$.

(b) Introduce the interference test gases listed in Table 30A–3 in section 17.0 into the measurement system separately or as a mixture. The interference test gases HCl and NO must be introduced as a mixture. The interference test gases must be introduced into the sampling system at the probe such that the interference gas mixtures pass through all filters, scrubbers, conditioners, and other components as would be configured for normal sampling.

(c) The interference test must be performed using $HgCl_2$, and each interference test gas (or gas mixture) must be evaluated in triplicate. This is accomplished by measuring the Hg response first with only the $HgCl_2$ gas present and then when adding the interference test gas(es) while maintaining the $HgCl_2$ concentration of the test stream constant. It is important that the equipment used to conduct the interference test be of sufficient quality so as to be capable of blending the $HgCl_2$ and interference gases while maintaining the Hg concentration constant. Gas blending system or manifolds may be used.

(d) The duration of each test should be for a sufficient period of time to ensure the Hg measurement system surfaces are conditioned and a stable output is obtained. Measure the Hg response of the analyzer to these gases in μg/m3. Record the responses and determine the overall interference response using Table 30A–4 in section 17.0 and the equations presented in section 12.11. The specification in section 13.4 must be met.

(e) A copy of these data, including the date completed and a signed certification, must be included with each test report. The intent of this test is that the interference test results are intended to be valid for the life of the system. As a result, the Hg measurement system should be operated and tested in a configuration consistent with the configuration that will be used for field applications. However, if the system used for field testing is not consistent with the system that was interference-tested, the interference test must be repeated before it is used for any field applications. Examples of such conditions include, but are not limited to: major changes in dilution ratio (for dilution based systems), changes in catalyst materials, changes in filtering device design or materials, changes in probe design or configuration, and changes in gas conditioning materials or approaches.

9.0 Quality Control

What quality control measures must I take?

The table which follows is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the run data, must be documented and included in the test report.

SUMMARY TABLE OF QA/QC REQUIREMENTS

Status[1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S	Identify Data User	Regulatory Agency or other primary end user of data.	Before designing test..	
M	Analyzer Design	Analyzer range	Sufficiently >high-level gas to allow determination of system calibration error.	
S	Analyzer resolution or sensitivity.	<2.0 % of full-scale range.	Manufacturer design..	
S	Interference response.	Overall response ≤3% of calibration span. Alternatively, overall response ≤0.3 $\mu g/m^3$.		
M	Calibration Gases	Traceability protocol	Validation of concentration required.	
M	High-level Hg^0 gas	Equal to the calibration span.	Each calibration error test..	
M	Mid-level Hg^0 gas	40 to 60% of calibration span.	Each calibration error test..	
M	Low-level Hg^0 gas	10 to 30% of calibration span.	Each calibration error test..	
M	High-level $HgCl_2$ gas	Equal to the calibration span.	Each system integrity check (if it better represents C_{native} than the mid level gas)..	
M	Mid-level $HgCl_2$	40 to 60% of calibration span.	Each system gas integrity check (if it better represents C_{native} than the high level gas)..	
M	Zero gas	Each system integrity check..		
M	Dynamic spike gas ($C_{native} \geq 1\ \mu g/m^3$).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 150 to 200% of the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
M	Dynamic spike gas ($C_{native} < 1\ \mu g/m^3$).	A high-concentration $HgCl_2$ gas, used to produce a spiked sample concentration that is 1 to 2 $\mu g/m^3$ above the native concentration.	Pre-test; dynamic spiking not required until 1/1/09..	
S	Data Recorder Design.	Data resolution	≤0.5% of full-scale	Manufacturer design.
M	Sample Extraction	Probe material	Inert to sample constituents (e.g., PFA Teflon, or quartz if stack >500 °F).	Each run.
M	Sample Extraction	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point, by heating prior to moisture removal. For wet-basis analyzers, keep sample above dew point at all times, by heating or dilution.	Each run.
M	Sample Extraction	Calibration valve material.	Inert to sample constituents (e.g., PFA Teflon or PFA Teflon coated).	Each test.
S	Sample Extraction	Sample pump material.	Inert to sample constituents	Each test.
M	Sample Extraction	Manifold material	Inert to sample constituents	Each test.

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status[1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
M	Particulate Removal	Filter inertness	Pass calibration error check	Each calibration error check.
M	System Calibration Performance.	System calibration error (CE) test.	CE $\leq$5.0 % of the calibration span for the low-, mid-or high-level Hg^0 calibration gas. Alternative specification: $\leq$0.5 $\mu g/m^3$ absolute difference between system response and reference value.	Before initial run and after a failed system integrity check or drift test.
M	System Calibration Performance.	System integrity check.	Error $\leq$5.0% of the calibration span for the zero and mid- or high-level $HgCl_2$ calibration gas. Alternative specification: $\leq$0.5 $\mu g/m^3$ absolute difference between system response and reference value.	Before initial run, after each run, at the beginning of subsequent test days, and after a failed system integrity check or drift test.
M	System Performance	System response time.	Used to determine minimum sampling time per point.	During initial 3-point system calibration error test.
M	System Performance	Drift	$\leq$3.0% of calibration span for the zero and mid- or high-level gas. Alternative specification: $\leq$0.3 $\mu g/m^3$ absolute difference between pre- and post-run system calibration error percentages..	At least once per test day.
M	System Performance	Minimum sampling time.	The greater of two times the system response time or 10 minutes. Concentrating systems must also include at least 4 cycles.	Each sampling point.
M	System Performance	Percentage spike recovery and relative standard deviation.	Percentage spike recovery, at the target level: 100 ±10%. Relative standard deviation: $\leq$5 percent ... Alternative specification: absolute difference between calculated and measured spike values $\leq$0.5 $\mu g/m^3$.	Before initial run; dynamic spiking not required until 1/1/09.
M	Sample Point Selection.	Number and Location of Sample Points.	For emission testing applications, use 12 points, located according to Method 1 in appendix A–1 to this part, unless the results of a stratification test allow fewer points to be used.	Prior to first run.
	For Part 60 RATAs, follow the procedures in Performance Specification 2, section 8.1.3, and for Part 75 RATAs, follow the procedures in section 6.5.6 of appendix A to Part 75. That is: • At *any* test location, you may use 3 sample points located at 16.7, 50.0, and 83.3% of a “long” measurement line passing through the centroidal area; or • At *any* test location, you may use 6 sample points along a diameter, located according to Method 1 (Part 75 RATAs, only); or			

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status[1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
	• At a location where stratification is not expected and the measurement line is >2.4 m (7.8 ft), you may use 3 sample points located along a "short" measurement line at 0.4, 1.0, and 2.0 m from the stack or duct wall or, for Part 75 only, sample points may be located at 4.4, 14.6, and 29.6% of the measurement line; or • After a wet scrubber or at a point where dissimilar gas streams are combined, either locate 3 sample points along the "long" measurement line or locate 6 Method 1 points along a diameter (Part 75, only), unless the results of a stratification test allow you to use a "short" 3-point measurement line or to sample at a single point. • If it can be demonstrated that stack gas concentration is ≤3 μg/m³, then the test site is exempted from stratification testing. Use the 3-point "short" measurement line if the stack diameter is >2.4 m (7.8 ft) and the 3-point "long" line for stack diameters ≤2.4 m (7.8 ft).			

SUMMARY TABLE OF QA/QC REQUIREMENTS—Continued

Status[1]	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
A	Sample Point Selection	Stratification Test (See section 8.1.3)..	If the Hg concentration[2] at each traverse point during the stratification test is: • Within ±5% of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±5% of mean, but is within ±10% of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method.. Alternatively, if the Hg concentration at each point is:. • Within ±0.2 μg/m³ of mean, use 1-point sampling (at the point closest to the mean); or. • Not within ±0.2 μg/m³ of mean, but is within ±0.5 μg/m³ of mean, use 3-point sampling. Locate points according to section 8.1.3.2.2 of this method..	Prior to first run. Prior to 1/1/09, you may (1) forgo stratification testing and use 3 sampling points (as per section 8.1.3.2.2) or (2) perform a SO_2 stratification test (see sections 6.5.6.1 and 6.5.6.3 of appendix A to part 75), in lieu of a Hg stratification test. If the test location is unstratified or minimally stratified for SO_2, it can be considered unstratified or minimally stratified for Hg also.
M	Data Recording	Frequency	Once per cycle	During run.
S	Data Parameters	Sample concentration and calibration span.	All analyzer readings during each run within calibration span.	Each run.
M	Data Parameters	Sample concentration and calibration span.	All analyzer readings during dynamic spiking tests within 120% of calibration span.	Each spike injection.
M	Data Parameters	Sample concentration and calibration span.	Average Hg concentration for the run ≤calibration span.	Each run.

[1] M = Mandatory; S = Suggested; A = Alternative.

[2] These may either be the unadjusted Hg concentrations or concentrations normalized to account for temporal variations.

10.0 Calibration and Standardization

What measurement system calibrations are required?

Your analyzer must be calibrated with Hg° standards. The initial 3-point system calibration error test described in section 8.2.4 is required before you start the test. Also, prior to and following test runs, the two-point system integrity checks described in sections 8.2.5 and 8.2.8 are required. On and after January 1, 2009, the pre-test dynamic spiking procedure described in section 8.2.7 is also required to verify that the accuracy of the measurement system is suitable and not adversely affected by the flue gas matrix.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

You must follow the procedures for calculations and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B_{ws} = Moisture content of sample gas as measured by Method 4 in Appendix A–3 to this part, percent/100.

C_{avg} = Average unadjusted Hg concentration for the test run, as indicated by the data recorder μg/m³.

$\bar{C}_{baseline}$ = Average Hg concentration measured before and after dynamic spiking injections, μg/m³.

C_d = Hg concentration, dry basis, μg/m³.

C_{dif} = Absolute value of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

$C_{dif\ avg}$ = Average of the 3 absolute values of the difference between the measured Hg concentrations of the reference $HgCl_2$ calibration gas, with and without the individual or combined interference gases, μg/m³.

C_{gas} = Average Hg concentration in the effluent gas for the test run, adjusted for system calibration error, μg/m³.

C_{int} = Measured Hg concentration of the reference $HgCl_2$ calibration gas plus the individual or combined interference gases, μg/m^3.

C_m = Average of pre- and post-run system integrity check responses for the upscale (i.e., mid- or high-level) calibration gas, μg/m^3.

C_{ma} = Actual concentration of the upscale (i.e., mid- or high-level) calibration gas used for the system integrity checks, μg/m^3.

C_0 = Average of pre- and post-run system integrity check responses from the zero gas, μg/m^3.

C_{native} = Vapor phase Hg concentration in the source effluent, μg/m^3.

C_{ref} = Measured Hg concentration of the reference $HgCl_2$ calibration gas alone, in the interference test, μg/m^3.

C_s = Measured concentration of a calibration gas (zero-, low-, mid-, or high-level), when introduced in system calibration mode, μg/m^3.

C_{spike} = Actual Hg concentration of the spike gas, μg/m^3.

C^*_{spike} = Hg concentration of the spike gas required to achieve a certain target value for the spiked sample Hg concentration, μg/m^3.

C_{ss} = Measured Hg concentration of the spiked sample at the target level, μg/m^3.

C^*_{ss} = Expected Hg concentration of the spiked sample at the target level, μg/m^3.

C_{target} = Target Hg concentration of the spiked sample, μg/m^3.

$C_{Tnative}$ = Measured tracer gas concentration present in native effluent gas, ppm.

C_{Tdir} = Tracer gas concentration injected with spike gas, ppm.

C_{Tv} = Diluted tracer gas concentration measured in a spiked sample, ppm.

C_v = Certified Hg° or $HgCl_2$ concentration of a calibration gas (zero, low, mid, or high), μg/m^3.

C_w = Hg concentration measured under moist sample conditions, wet basis, μg/m^3.

CS = Calibration span, μg/m^3.

D = Zero or upscale drift, percent of calibration span.

DF = Dilution factor of the spike gas, dimensionless.

I = Interference response, percent of calibration span.

Q_{probe} = Total flow rate of the stack gas sample plus the spike gas, liters/min.

Q_{spike} = Flow rate of the spike gas, liters/min.

R_i = Individual injection spike recovery, %.

$\bar{R}$ = Mean value of spike recoveries at a particular target level, %.

RSD = Relative standard deviation, %;.

SCE = System calibration error, percent of calibration span.

SCE_i = Pre-run system calibration error during the two-point system integrity check, percent of calibration span.

SCE_f = Post-run system calibration error during the two-point system integrity check, percent of calibration span.

12.2 System Calibration Error. Use Equation 30A–1 to calculate the system calibration error. Equation 30A–1 applies to: 3–point system calibration error tests performed with Hg° standards; and pre- and post-run two-point system integrity checks performed with $HgCl_2$.

$$SCE = \frac{C_s - C_v}{CS} \times 100 \qquad \text{Eq. 30A-1}$$

12.3 Drift Assessment. Use Equation 30A–2 to separately calculate the zero and upscale drift for each test run.

$$D = \left| SCE_f - SCE_i \right| \qquad \text{Eq. 30A-2}$$

12.3 Effluent Hg Concentration. For each test run, calculate C_{avg}, the arithmetic average of all valid Hg concentration values recorded during the run. Then, adjust the value of C_{avg} for system calibration error, using Equation 30A–3.

$$C_{gas} = (C_{avg} - C_0)\ \frac{C_{ma}}{C_m - C_0} \qquad \text{Eq. 30A-3}$$

12.4 Moisture Correction. Use Equation 30A–4a if your measurements need to be corrected to a dry basis.

$$C_d = \frac{C_w}{1 - B_{ws}} \qquad \text{Eq. 30A-4a}$$

Use Equation 30A–4b if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30A-4b}$$

12.5 Dynamic Spike Gas Concentrations. Use Equation 30A–5 to determine the spike gas concentration needed to produce a spiked sample with a certain “target” Hg concentration.

$$C^{*}_{spike} = DF(C_{target} - C_{native}) + C_{native} \qquad \text{Eq. 30A-5}$$

12.6 Spiked Sample Concentration. Use Equation 30A–6 to determine the expected or theoretical Hg concentration of a spiked sample.

$$C^{*}_{ss} = C_{native} + \frac{(C_{spike} - C_{native})}{DF} \qquad \text{Eq. 30A-6}$$

12.7 Spike Recovery. Use Equation 30A–7 to calculate the percentage recovery of each spike.

$$R = \frac{DF\ (C_{ss} - C_{native}) + C_{native}}{C_{spike}} \times 100\% \qquad \text{Eq. 30A-7}$$

12.8 Relative Standard Deviation. Use Equation 30A–8 to calculate the relative standard deviation of the individual percentage spike recovery values from the mean.

$$RSD = \frac{100\%}{\bar{R}} \sqrt{\frac{\sum_{i=1}^{n} (R_i - \bar{R})^2}{n - 1}} \qquad \text{Eq. 30A-8}$$

12.9 Spike Dilution Factor. Use Equation 30A–9 to calculate the spike dilution factor, using either direct flow measurements or tracer gas measurements.

$$DF = \frac{Q_{probe}}{Q_{spike}} = \frac{C_{Tdir} - C_{Tnative}}{C_{Ttv} - C_{Tnative}} \qquad \text{Eq. 30A-9}$$

12.10 Native Concentration. For spiking procedures that inject blank or carrier gases (at the spiking flow rate, Q_{spike}) between spikes, use Equation 30A–10 to calculate the native concentration.

$$C_{native} = \frac{\bar{C}_{baseline} DF}{DF - 1} \qquad \text{Eq. 30A-10}$$

For spiking procedures that halt all injections between spikes, the native concentration equals the average baseline concentration (see Equation 30A–11).

$$C_{native} = \bar{C}_{baseline} \qquad \text{Eq. 30A-11}$$

12.11 Overall Interference Response. Use equation 30A–12 to calculate the overall interference response.

$$I = \frac{\sum C_{difavg}}{CS} \times 100 \qquad \text{Eq. 30A-12}$$

Where, for each interference gas (or mixture):

$$C_{difavg} = \frac{\sum_{1}^{3} C_{dif}}{3} \qquad \text{Eq. 30A-13}$$

$$C_{dif} = \left| C_{ref} - C_{int} \right| \qquad \text{Eq. 30A-14}$$

13.0 Method Performance

13.1 System Calibration Error Test. This specification applies to the 3-point system calibration error tests using Hg^0. At each calibration gas level tested (low-, mid-, or high-level), the calibration error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $| C_s - C_v | \leq 0.5\ \mu g/m^3$.

13.2 System Integrity Checks. This specification applies to all pre- and post-run 2-point system integrity checks using $HgCl_2$ and zero gas. At each calibration gas level tested (zero and mid- or high-level), the error must be within ±5.0 percent of the calibration span. Alternatively, the results are acceptable if $| C_s - C_v | \leq 0.5\ \mu g/m^3$.

13.3 Drift. For each run, the low-level and upscale drift must be less than or equal to 3.0 percent of the calibration span. The drift is also acceptable if the pre- and post-run system integrity check responses do not differ by more than $0.3\ \mu g/m^3$ (i.e., $| C_{s\ post\text{-}run} - C_{s\ pre\text{-}run} | \leq 0.3\ \mu g/m^3$).

13.4 Interference Test. Summarize the results following the format contained in Table 30A–4. For each interference gas (or mixture), calculate the mean difference between the measurement system responses with and without the interference test gas(es). The overall interference response for the analyzer that was used for the test (calculated according to Equation 30A–12), must not be greater than 3.0 percent of the calibration span used for the test (see section 8.6). The results of the interference test are also acceptable if the sum of the absolute average differences for all interference gases (i.e., $\Sigma C_{dif\ avg}$) does not exceed $0.3\ \mu g/m^3$.

13.5 Dynamic Spiking Test. For the pretest dynamic spiking, the mean value of the percentage spike recovery must be 100 ±10 percent. In addition, the relative standard deviation (RSD) of the individual percentage spike recovery values from the mean must be ≤5.0 percent. Alternatively, if the mean percentage recovery is not met, the results are acceptable if the absolute difference between the theoretical spiked sample concentration (see section 12.6) and the actual average value of the spiked sample concentration is $\leq 0.5\ \mu g/m^3$.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc.*

2. EPA Traceability Protocol for Qualification and Certification of Oxidized Mercury Gas Generators, expected publication date December 2008, see *www.epa.gov/ttn/emc.*

3. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, expected revision publication date December 2008, see *www.epa.gov/ttn/emc.*

17.0 Figures and Tables

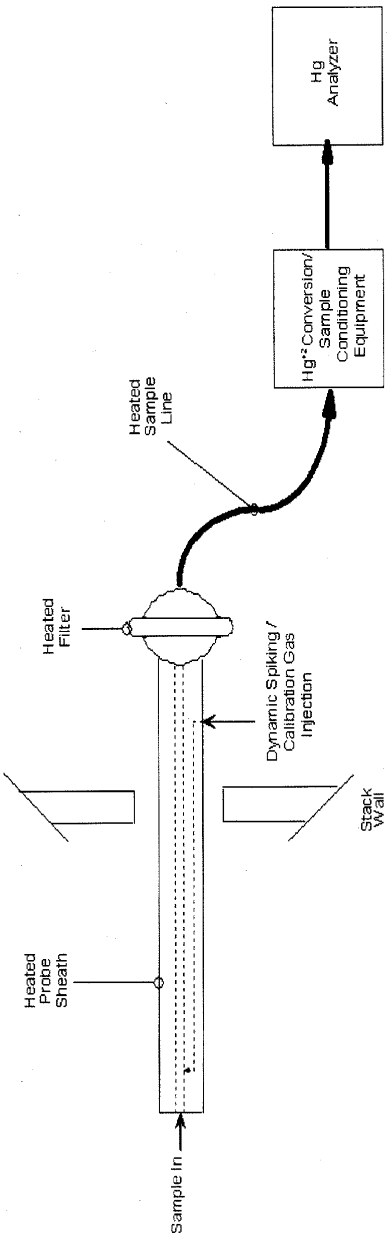


Figure 30A-1: Example Hg Measurement System

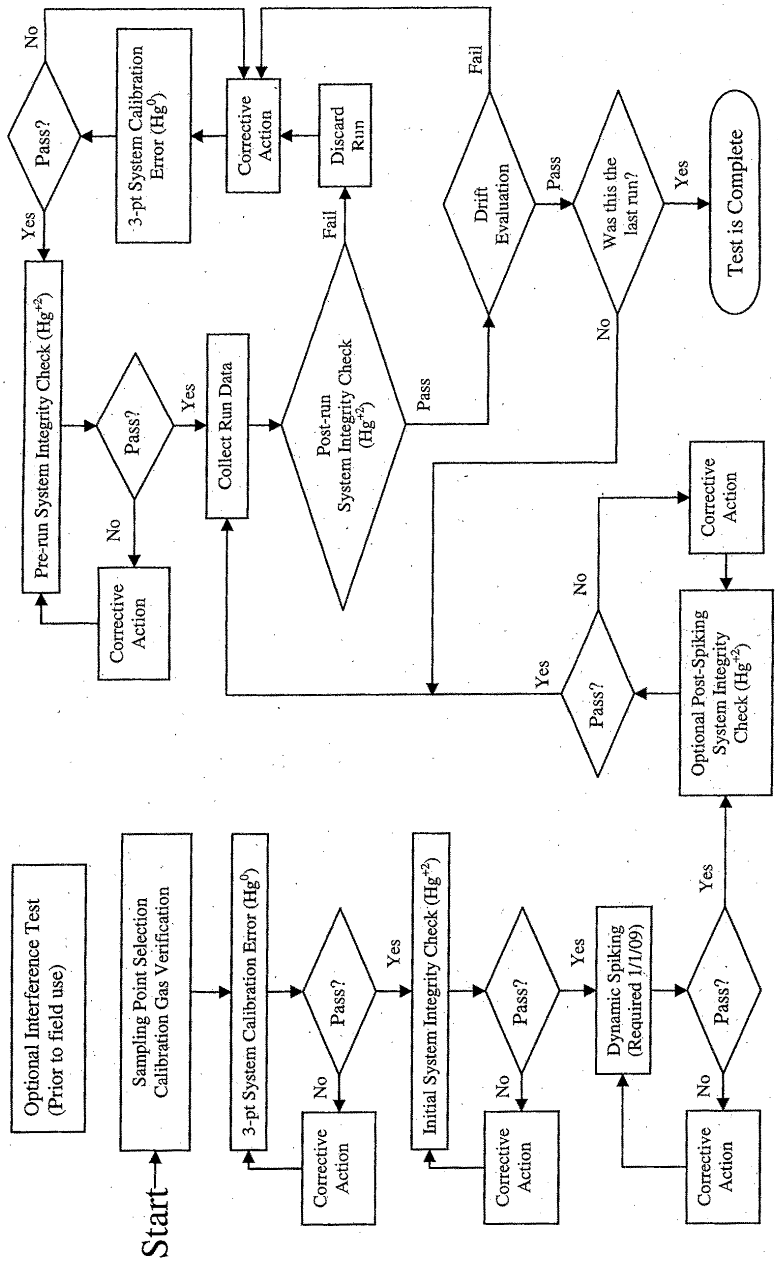


Figure 30A-2. Testing Flow Chart

Table 30A-1: 3-Point System Calibration Error Tests

Facility name: ____________________
Unit(s) tested:____________________
Test personnel:____________________
Date: ____________________________
Time: ____________________________

Test Runs Covered: ____________________
Analyzer make & model no.____________
Serial no.____________________________
Calibration span (CS):_________________
System response time: ________________

Calibration Gas Level	Certified Gas Concentration ($\mu g/m^3$) A	System Response ($\mu g/m^3$) B	Absolute Difference $\lvert A-B \rvert$	Calibration Error (% of calibration span) $\frac{[\lvert A-B \rvert]*100}{CS}$
Low				
Mid				
High				

Table 30A-2: System Integrity Check and Drift Data

Facility name:_____________ Analyzer make & model: _______________

Unit(s) tested: _____________ Serial number: ________________________

Test personnel: _____________ Run number(s) covered:________________

Date(s): ___________________ Calibration span: ______________________

Calibration Gas Level (zero, mid, or high)	Certified Calibration Gas Value (μg/m^3)	Initial System Response (μg/m^3)	Final System Response (μg/m^3)	Absolute Difference (μg/m^3)	Drift (% of calibration span)

TABLE 30A–3—INTERFERENCE CHECK GAS CONCENTRATIONS

Potential interferent gas [1]	Concentration, tentative—(balance N_2)
CO_2	15% ±1% CO_2
CO	100 ±20 ppm
HCl [2]	100 ±20 ppm
NO [2]	250 ±50 ppm
SO_2	200 ±20 ppm
O_2	3% ±1% O_2
H_2O	10% ±1% H_2O
Nitrogen	Balance
Other.	

[1] Any of these specific gases can be tested at a lower level if the manufacturer has provided reliable means for limiting or scrubbing that gas to a specified level.

[2] HCl and NO must be tested as a mixture.

Table 30A-4: Example Interference Test Data Sheet

Date of Test:
Analyzer Type:
Model No.:
Serial No.:
Calibration Span:
Test Organization:
Test Personnel:

Interference Gas	Hg Concentration (μg/m³)	Hg Concentration (μg/m³) w/Interference Gas	Absolute Difference (μg/m³)	Average Absolute Difference (μg/m³)
Sum of Responses				
% of Calibration Span				

Table 30A-5: Example Dynamic Spiking Data Sheet

Facility name: ____________________
Unit(s) tested: ____________________
Analyzer make & model: ______________
Serial number: ____________________
Calibration span: _______________ µg/m^3

Date: ________ Time: ________
Test personnel: __________________
Estimated native Hg concentration: _______ µg/m^3
Estimated unspiked sample flow rate: _______ lpm
Estimated spike gas flow rate: _______ lpm

Q_{probe} (lpm)	Q_{spike} (lpm)	DF[1]	Target Level[2]		C_{native} (µg/m^3)			Actual Values		% Spike Recovery
			C^*_{spike} (µg/m^3)	C^*_{ss} (µg/m^3)	Pre	Post	Avg.	C_{spike} (µg/m^3)	C_{ss} (µg/m^3)	
									Avg.	
									RSD	

---

[1] DF must be ≥ 5

[2] C^*_{ss}/C_{native} must be ≥ 1.5 and ≤ 2.0, where C_{native} and C^*_{ss} are <u>estimated</u> values

METHOD 30B—DETERMINATION OF TOTAL VAPOR PHASE MERCURY EMISSIONS FROM COAL-FIRED COMBUSTION SOURCES USING CARBON SORBENT TRAPS

1.0 Scope and Application

What is Method 30B?

Method 30B is a procedure for measuring total vapor phase mercury (Hg) emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known and acceptable quality for each testing program. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need, but instead refers to other test methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional methods which are found in Appendices A–1 and A–3 to this part:

(a) Method 1—Sample and Velocity Traverses for Stationary Sources.

(b) Method 4—Determination of Moisture Content in Stack Gases.

(c) Method 5—Determination of Particulate Matter Emissions from Stationary Sources

1.1 Analytes. What does this method determine? This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, including elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in micrograms per dry standard cubic meter (µg/dscm).

Analyte	CAS No.	Analytical range and sensitivity
Elemental Hg (Hg^0) ..	7439–97–6	Typically 0.1 µg/dscm to >50 µg/dscm.
Oxidized Hg (Hg^{+2}) ...	....	(Same)

1.2 Applicability. When is this method required? Method 30B is a reference method for relative accuracy test audits (RATAs) of vapor phase Hg CEMS and sorbent trap monitoring systems installed at coal-fired boilers and is also appropriate for Hg emissions testing at such boilers. It is intended for use only under relatively low particulate conditions (i.e., sampling after all pollution control devices); in cases where significant amounts of particle-bound Hg may be present, an isokinetic sampling method for Hg should be used. Method 30B may also be specified by New Source Performance Standards (NSPS), National Emission Standards for Hazardous Air Pollutants (NESHAP), emissions trading programs, State Implementation Plans (SIPs), and operating permits that require measurement of Hg concentrations in stationary source emissions, either to determine compliance with an applicable emission standard or limit, or to conduct RATAs of Hg CEMS and sorbent trap monitoring systems.

1.3 Data Quality Objectives (DQO). How good must my collected data be? Method 30B has been designed to provide data of high and known quality for Hg emissions testing and for RATA testing of Hg monitoring systems, including CEMS and sorbent trap monitors. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emissions levels and in the actual emissions matrix encountered. To meet this objective, NIST-traceable calibration standards must be used and method performance tests are required.

2.0 Summary of Method

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack sorbent media traps at an appropriate flow rate. Collection of mercury on the sorbent media in the stack mitigates potential loss of mercury during transport through a probe/sample line. For each test run, paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data. A field recovery test which assesses recovery of an elemental Hg spike to determine measurement bias is also used to verify data acceptability. The sorbent traps are recovered from the sampling system, prepared for analysis as needed, and analyzed by any suitable determinative technique that can meet the performance criteria.

3.0 Definitions

3.1 *Analytical System* is the combined equipment and apparatus used to perform sample analyses. This includes any associated sample preparation apparatus e.g., digestion equipment, spiking systems, reduction devices, etc., as well as analytical instrumentation such as UV AA and UV AF cold vapor analyzers.

3.2 *Calibration Standards* are the Hg containing solutions prepared from NIST traceable standards and are used to directly calibrate analytical systems.

3.3 *Independent Calibration Standard* is a NIST traceable standard obtained from a source or supplier independent of that for the calibration standards and is used to confirm the integrity of the calibration standards used.

3.4 *Method Detection Limit (MDL)* is the lowest mass of Hg greater than zero that can be estimated and reported by your candidate analytical technique. The MDL is statistically derived from replicate low level measurements near your analytical instrument's detection level.

3.5 *NIST* means the National Institute of Standards and Technology, located in Gaithersburg, Maryland.

3.6 *Run* means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

3.7 *Sorbent Trap* means a cartridge or sleeve containing a sorbent media (typically activated carbon treated with iodine or some other halogen) with multiple sections separated by an inert material such as glass wool. These sorbent traps are optimized for the quantitative capture of elemental and oxidized forms of Hg and can be analyzed by multiple techniques.

3.8 *Test* refers to the series of runs required by the applicable regulation.

3.9 *Thermal Analysis* means an analytical technique where the contents of the sorbent traps are analyzed using a thermal technique (desorption or combustion) to release the captured Hg in a detectable form for quantification.

3.10 *Wet Analysis* means an analytical technique where the contents of the sorbent tube are first leached or digested to quantitatively transfer the captured Hg to liquid solution for subsequent analysis.

4.0 Interferences

Interferences may result from the sorbent trap material used as well as from the measurement environment itself. The iodine present on some sorbent traps may impart a negative measurement bias. High levels of sulfur trioxide (SO_3) are also suspected to compromise the performance of sorbent trap Hg capture. These, and other, potential interferences are assessed by performing the analytical matrix interference, Hg^0 and $HgCl_2$ analytical bias and field recovery tests.

5.0 Safety

What safety measures should I consider when using this method? This method may require you to work with hazardous materials and in hazardous conditions. You are encouraged to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual. Occupational Safety and Health Administration (OSHA) regulations concerning use of compressed gas cylinders and noxious gases may apply.

5.1 Site Hazards. Prior to applying these procedures/specifications in the field, the potential hazards at the test site should be considered; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment.

5.2 Laboratory Safety. Policies should be in place to minimize risk of chemical exposure and to properly handle waste disposal in the laboratory. Personnel shall wear appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory.

5.3 Reagent Toxicity/Carcinogenicity. The toxicity and carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment and this method does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the Material Safety Data Sheet (MSDS) for each chemical used.

5.4 Waste Disposal. Any waste generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

6.0 Equipment and Supplies

The following list is presented as an example of key equipment and supplies likely required to measure vapor-phase Hg using a sorbent trap sampling system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required.

6.1 Sorbent Trap Sampling System. A typical sorbent trap sampling system is shown in Figure 30B–1 in section 17.0. The sorbent trap sampling system shall include the following components:

6.1.1 Sorbent Traps. The sorbent media used to collect Hg must be configured in a trap with at least two distinct segments or sections, connected in series, that are amenable to separate analyses. section 1 is designated for primary capture of gaseous Hg. section 2 is designated as a backup section for determination of vapor phase Hg breakthrough. Each sorbent trap must be inscribed or otherwise permanently marked with a unique identification number, for tracking purposes. The sorbent media may be any collection material (e.g., carbon, chemically-treated filter, etc.) capable of quantitatively capturing and recovering for subsequent analysis, all gaseous forms of Hg in the emissions from the intended application. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in this method as well as the sorbent's vapor phase

Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. The sorbent media must be obtained from a source that can demonstrate their quality assurance and quality control (see section 7.2). The paired sorbent traps are supported on a probe (or probes) and inserted directly into the flue gas stream.

6.1.2 Sampling Probe Assembly. Each probe assembly shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of or within the probe such that the gas sampled enters the trap directly. Each probe/sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent trap(s). Auxiliary heating is required only where the stack temperature is too low to prevent condensation. Use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located to ensure representative Hg monitoring.

6.1.3 Moisture Removal Device. A moisture removal device or system shall be used to remove water vapor from the gas stream prior to entering dry gas flow metering devices.

6.1.4 Vacuum Pump. Use a leak-tight, vacuum pump capable of operating within the system's flow range.

6.1.5 Gas Flow Meter. A gas flow meter (such as a dry gas meter, thermal mass flow meter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2 percent and must be calibrated at selected flow rates across the range of sample flow rates at which the sampling train will be operated. The gas flow meter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

6.1.6 Sample Flow Rate Meter and Controller. Use a flow rate indicator and controller for maintaining necessary sampling flow rates.

6.1.7 Temperature Sensor. Same as section 6.1.1.7 of Method 5 in Appendix A–3 to this part.

6.1.8 Barometer. Same as section 6.1.2 of Method 5 in Appendix A–3 to this part.

6.1.9 Data Logger (optional). Device for recording associated and necessary ancillary information (e.g., temperatures, pressures, flow, time, etc.).

6.2 Gaseous Hg^0 Sorbent Trap Spiking System. A known mass of gaseous Hg^0 must be either present on or spiked onto the first section of sorbent traps in order to perform the Hg^0 and $HgCl_2$ analytical bias test and the field recovery study. Any approach capable of quantitatively delivering known masses of Hg^0 onto sorbent traps is acceptable. Several spiking technologies or devices are available to meet this objective. Their practicality is a function of Hg mass spike levels. For low levels, NIST-certified or NIST-traceable gas generators or tanks may be suitable. An alternative system, capable of delivering almost any mass required, makes use of NIST-certified or NIST-traceable Hg salt solutions (e.g., $HgCl_2$, $Hg(NO_3)_2$). With this system, an aliquot of known volume and concentration is added to a reaction vessel containing a reducing agent (e.g., stannous chloride); the Hg salt solution is reduced to Hg^0 and purged onto the sorbent trap using an impinger sparging system. When available, information on example spiking systems will be posted at *http://www.epa.gov/ttn/emc.*

6.3 Sample Analysis Equipment. Any analytical system capable of quantitatively recovering and quantifying total Hg from the sorbent media selected is acceptable provided that the analysis can meet the performance criteria described in this method. Example recovery techniques include acid leaching, digestion, and thermal desorption/direct combustion. Example analytical techniques include, but are not limited to, ultraviolet atomic fluorescence (UV AF), ultraviolet atomic absorption (UV AA) with and without gold trapping, and X-ray fluorescence (XRF) analysis.

6.3 Moisture Measurement System. If correction of the measured Hg emissions for moisture is required (see section 8.3.3.7), either Method 4 in Appendix A–3 to this part or other moisture measurement methods approved by the Administrator will be needed to measure stack gas moisture content.

7.0 Reagents and Standards

7.1 Reagents and Standards. Only NIST-certified or NIST-traceable calibration standards, standard reference materials, and reagents shall be used for the tests and procedures required by this method.

7.2 Sorbent Trap Media. The sorbent trap media shall be prepared such that the material used for testing is of known and acceptable quality. Sorbent supplier quality assurance/quality control measures to ensure appropriate and consistent performance such as sorptive capacity, uniformity of preparation treatments, and background levels shall be considered.

8.0 Sample Collection and Handling

This section presents the sample collection and handling procedures along with the pretest and on-site performance tests required by this method. Since you may choose different options to comply with certain performance criteria, each test report must identify the specific options selected and document the results with respect to the performance criteria of this method.

8.1 Selection of Sampling Sites and Sampling Points. What sampling site and sampling points do I select? Same as section 8.1 of Method 30A of this appendix.

8.2 Measurement System Performance Tests. What performance criteria must my measurement system meet? The following laboratory and field procedures and associated criteria of this section are designed to ensure (1) selection of a sorbent and analytical technique combination capable of quantitative collection and analysis of gaseous Hg, (2) collection of an adequate amount of Hg on each sorbent trap during field tests, and (3) adequate performance of the method for each test program: The primary objectives of these performance tests are to characterize and verify the performance of your intended analytical system and associated sampling and analytical procedures, and to define the minimum amount of Hg (as the sample collection target) that can be quantified reliably.

(a) Analytical Matrix Interference Test;

(b) Determination of Minimum Sample Mass;

(c) Hg^0 and $HgCl_2$ Analytical Bias Test;

(d) Determination of Nominal Sample Volume;

(e) Field Recovery Test.

8.2.1 Analytical Matrix Interference Test and Minimum Sample Dilution.

(a) The analytical matrix interference test is a laboratory procedure. It is required only if you elect to use a liquid digestion analytical approach and needs to be performed only once for each sorbent material used. The purpose of the test is to verify the presence or absence of known and potential analytical matrix interferences, including the potential negative bias associated with iodine common to many sorbent trap materials. The analytical matrix interference test determines the minimum dilution (if any) necessary to mitigate matrix effects on the sample digestate solutions.

(b) The result of the analytical matrix interference test, i.e., the minimum sample dilution required (if any) for all sample analyses, is used to establish the minimum sample mass needed for the Hg^0 and $HgCl_2$ analytical bias test and to determine the nominal sample volume for a test run. The analytical matrix interference test is sorbent material-specific and shall be performed for each sorbent material you intend to use for field sampling and analysis. The test shall be performed using a mass of sorbent material comparable to the sorbent mass typically used in the first section of the trap for sampling. Similar sorbent materials from different sources of supply are considered to be different materials and must be tested individually. You must conduct the analytical matrix interference test for each sorbent material prior to the analysis of field samples.

8.2.1.1 Analytical Matrix Interference Test Procedures. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for field samples. Analyze the digestate according to your intended analytical conditions at the least diluted level you intend to use for sample analysis (e.g., undiluted, 1 in 10 dilution, etc.). Determine the Hg concentration of the undiluted digestate solution. Prepare a series of solutions with a fixed final volume containing graduated aliquots of the sample digestate and, a fixed aliquot of a calibration standard (with the balance being Hg-free reagent or H_20) to establish solutions of varied digestate dilution ratio (e.g., 1:2, 1:5, 1:10, 1:100, etc.—see example in section 8.2.1.3, below). One of these solutions should contain only the aliquot of the calibration standard in Hg-free reagent or H_2O. This will result in a series of solutions where the amount of Hg is held relatively constant and only the volume of digestate diluted is varied. Analyze each of these solutions following intended sample analytical procedures and conditions, determining the concentration for each solution.

8.2.1.2 Analytical Matrix Interference Test Acceptance Criteria. Compare the measured concentration of each solution containing digestate to the measured concentration of the digestate-free solution. The lowest dilution ratio of any solution having a Hg concentration within ±5 percent of the digestate-free solution is the minimum dilution ratio required for analysis of all samples. If you desire to measure the digestate without dilution, the ±5 percent criterion must be met at a dilution ratio of at least 9:10 (i.e., ≥90% digestate).

8.2.1.3 Example Analytical Matrix Interference Test. An example analytical matrix interference test is presented below. Additional information on the conduct of the analytical matrix interference test will be posted at *http://www.epa.gov/ttn/emc*. Determine the most sensitive working range for the analyzer to be used. This will be a narrow range of concentrations. Digest and prepare for analysis a representative mass of sorbent material (unsampled) according to your intended laboratory techniques for sample preparation and analysis. Prepare a calibration curve for the most sensitive analytical region, e.g., 0.0, 0.5, 1.0, 3.0, 5.0, 10 ppb. Using the highest calibration standard, e.g., 10.0 ppb, prepare a series of solutions by adding successively smaller increments of the digestate to a fixed volume of the calibration standard and bringing each solution to a final fixed volume with mercury-free deionized water (diH_2O). To 2.0 ml of the calibration standard add 18.0, 10.0, 4.0, 2.0, 1.0, 0.2, and 0.0 ml of the digestate. Bring the final volume of each solution to a total volume of

20 ml by adding 0.0, 8.0, 14.0, 16.0, 17.0, 17.8, and 18.0 ml of diH_2O. This will yield solutions with dilution ratios of 9:10, 1:2, 1:5, 1:10, 1:20, 1:100, and 0:10, respectively. Determine the Hg concentration of each solution. The dilution ratio of any solution having a concentration that is within ±5 percent of the concentration of the solution containing 0.0 ml of digestate is an acceptable dilution ratio for analyzing field samples. If more than one solution meets this criterion, the one with the lowest dilution ratio is the minimum dilution required for analysis of field samples. If the 9:10 dilution meets this criterion, then no sample dilution is required.

8.2.2 Determination of Minimum Sample Mass. The minimum mass of Hg that must be collected per sample must be determined. This information is necessary in order to effectively perform the Hg^0 and $HgCl_2$ Analytical Bias Test, to estimate target sample volumes/sample times for test runs, and to ensure the quality of the measurements. The determination of minimum sample mass is a direct function of analytical technique, measurement sensitivity, dilutions, etc. This determination is required for all analytical techniques. Based on the analytical approach you employ, you should determine the most sensitive calibration range. Based on a calibration point within that range, you must consider all sample treatments (e.g., dilutions) to determine the mass of sample that needs to be collected to ensure that all sample analyses fall within your calibration curve.

8.2.2.1 Determination of Minimum Calibration Concentration or Mass. Based on your instrument's sensitivity and linearity, determine the calibration concentrations or masses that make up a representative low level calibration range. Verify that you are able to meet the multipoint calibration performance criteria in section 11.0 of this method. Select a calibration concentration or mass that is no less than 2 times the lowest concentration or mass in your calibration curve. The lowest point in your calibration curve must be at least 5, and preferably 10, times the Method Detection Limit (MDL), which is the minimum amount of the analyte that can be detected and reported. The MDL must be determined at least once for the analytical system using an MDL study such as that found in section 15.0 to Method 301 of appendix A to part 63 of this chapter.

NOTE TO SECTION 8.2.2.1: While it might be desirable to base the minimum calibration concentration or mass on the lowest point in the calibration curve, selecting a higher concentration or mass is necessary to ensure that all analyses of the field samples will fall within the calibration curve. Therefore, it is strongly recommended that you select a minimum calibration concentration or mass that is sufficiently above the lowest point of the calibration curve (see examples in sections 8.2.2.2.1 and 8.2.2.2.2 below).

8.2.2.2 Determination of Minimum Sample Mass. Based on your minimum calibration concentration or mass and other sample treatments including, but not limited to, final digestate volume and minimum sample dilution, determine the minimum sample mass. Consideration should also be given to the Hg levels expected to be measured in section 2 of the sorbent traps and to the breakthrough criteria presented in Table 9–1.

8.2.2.2.1 Example Determination of Minimum Sample Mass for Thermal Desorption Analysis. A thermal analysis system has been calibrated at five Hg mass levels: 10 ng, 20 ng, 50 ng, 100 ng, 200 ng, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 20 ng is selected as the minimum calibration mass. Because the entire sample is analyzed and there are no dilutions involved, the minimum sample mass is also 20 ng.

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criteria in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 50 ng) as the minimum calibration and sample mass.

8.2.2.2.2 Example Determination of Minimum Sample Mass for Acid Leachate/Digestate Analysis. A cold vapor analysis system has been calibrated at four Hg concentration levels: 2 ng/L, 5 ng, 10 ng/L, 20 ng/L, and shown to meet the calibration performance criteria in this method. Based on 2 times the lowest point in the calibration curve, 4 ng/L was selected as the minimum calibration concentration. The final sample volume of a digestate is nominally 50 ml (0.05 L) and the minimum dilution necessary was determined to be 1:100 by the Analytical Matrix Interference Test of section 8.2.1. The following calculation would be used to determine the minimum sample mass.

$$\text{Minimum sample mass} = (4\ \text{ng/L}) \times (0.05\ \text{L}) \times (100) = 20\ \text{ng}$$

NOTE: In this example, if the typical background (blank) Hg levels in section 2 were relatively high (e.g., 3 to 5 ng), a sample mass of 20 ng might not have been sufficient to ensure that the breakthrough criterion in Table 9–1 would be met, thereby necessitating the use of a higher point on the calibration curve (e.g., 10 ng/L) as the minimum calibration concentration.

8.2.3 Hg^0 and $HgCl_2$ Analytical Bias Test. Before analyzing any field samples, the laboratory must demonstrate the ability to recover and accurately quantify Hg^0 and $HgCl_2$

from the chosen sorbent media by performing the following analytical bias test for sorbent traps spiked with Hg^0 and $HgCl_2$. The analytical bias test is performed at a minimum of two distinct sorbent trap Hg loadings that will: (1) Represent the lower and upper bound of sample Hg loadings for application of the analytical technique to the field samples, and (2) be used for data validation.

8.2.3.1 Hg^0 and $HgCl_2$ Analytical Bias Test Procedures. Determine the lower and upper bound mass loadings. The minimum sample mass established in section 8.2.2.2 can be used for the lower bound Hg mass loading although lower Hg loading levels are acceptable. The upper bound Hg loading level should be an estimate of the greatest mass loading that may result as a function of stack concentration and volume sampled. As previously noted, this test defines the bounds that actual field samples must be within in order to be valid.

8.2.3.1.1 Hg^0 Analytical Bias Test. Analyze the front section of three sorbent traps containing Hg^0 at the lower bound mass loading level and the front section of three sorbent traps containing Hg^0 at the upper bound mass loading level. In other words, analyze each mass loading level in triplicate. You may refer to section 6.2 for spiking guidance. Prepare and analyze each spiked trap, using the same techniques that will be used to prepare and analyze the field samples. The average recovery for the three traps at each mass loading level must be between 90 and 110 percent. If multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.3.1.2 $HgCl_2$ Analytical Bias Test. Analyze the front section of three sorbent traps containing $HgCl_2$ at the lower bound mass loading level and the front section of three traps containing $HgCl_2$ at the upper bound mass loading level. $HgCl_2$ can be spiked as a gas, or as a liquid solution containing $HgCl_2$. However the liquid volume spiked must be <100 μL. Prepare and analyze each spiked trap, using the techniques that will be used to prepare and analyze the field samples. The average recovery for three traps at each spike concentration must be between 90 and 110 percent. Again, if multiple types of sorbent media are to be analyzed, a separate analytical bias test is required for each sorbent material.

8.2.4 Determination of Target Sample Volume. The target sample volume is an estimate of the sample volume needed to ensure that valid emissions data are collected (i.e., that sample mass Hg loadings fall within the analytical calibration curve and are within the upper and lower bounds set by the analytical bias tests). The target sample volume and minimum sample mass can also be determined by performing a diagnostic test run prior to initiation of formal testing.

Example: If the minimum sample mass is 50 ng and the concentration of mercury in the stack gas is estimated to be 2 μg/m³ (ng/L) then the following calculation would be used to determine the target sample volume:

Target Sample Volume = (50 ng) / (2 ng/L) = 25 L

NOTE TO SECTION 8.2.4: For the purposes of relative accuracy testing of Hg monitoring systems under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, when the stack gas Hg concentration is expected to be very low (<0.5 μg/dscm), you may estimate the Hg concentration at 0.5 μg/dscm.

8.2.5 Determination of Sample Run Time. Sample run time will be a function of minimum sample mass (see section 8.2.2), target sample volume and nominal equipment sample flow rate. The minimum sample run time for conducting relative accuracy test audits of Hg monitoring systems is 30 minutes and for emissions testing to characterize an emission source is 1 hour. The target sample run time can be calculated using the following example.

Example: If the target sample volume has been determined to be 25 L, then the following formula would be used to determine the sampling time necessary to acquire 25 L of gas when sampling at a rate of 0.4 L/min.

Sampling time (min) = 25 L / 0.4 L/min = 63 minutes

8.2.6 Field Recovery Test. The field recovery test provides a test program-specific verification of the performance of the combined sampling and analytical approach. Three sets of paired samples, one of each pair which is spiked with a known level of Hg, are collected and analyzed and the average recovery of the spiked samples is used to verify performance of the measurement system under field conditions during that test program. The conduct of this test requires an estimate or confirmation of the stack Hg concentrations at the time of testing.

8.2.6.1 Calculation of Pre-sampling Spiking Level. Determine the sorbent trap spiking level for the field recovery test using estimates of the stack Hg concentration, the target sample flow rate, and the planned sample duration. First, determine the Hg mass expected to be collected in section 1 of the sorbent trap. The pre-sampling spike must be within 50 to 150 percent of this expected mass.

Example calculation: For an expected stack Hg concentration of 5 ug/m³ (ng/L) a target sample rate of 0.40 liters/min, and a sample duration of 1 hour:

(0.40 L/min) * (60 min) * (5ng/L) = 120 ng

A Hg spike of 60 to 180 ng (50–150% of 120 ng) would be appropriate.

8.2.6.2 Procedures. Set up two identical sampling trains. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike Hg^0 onto the front section of the sorbent trap in the spiked train before sampling. The mass of Hg spiked shall be 50 to 150 percent of the mass expected to be collected with the unspiked train. Sample the stack gas with the two trains simultaneously using the same procedures as for the field samples (see section 8.3). The total sample volume must be within ±20 percent of the target sample volume for the field sample test runs. Analyze the sorbent traps from the two trains utilizing the same analytical procedures and instrumentation as for the field samples (see section 11.0). Determine the fraction of spiked Hg recovered (R) using the equations in section 12.7. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 85 and 115 percent.

NOTE TO SECTION 8.2.6.2: It is acceptable to perform the field recovery test concurrent with actual test runs (e.g., through the use of a quad probe). It is also acceptable to use the field recovery test runs as test runs for emissions testing or for the RATA of a Hg monitoring system under subpart UUUUU of part 63 of this chapter and Performance Specifications 12A and 12B in appendix B to this part, if certain conditions are met. To determine whether a particular field recovery test run may be used as a RATA run, subtract the mass of the Hg^0 spike from the total Hg mass collected in sections 1 and 2 of the spiked trap. The difference represents the mass of Hg in the stack gas sample. Divide this mass by the sample volume to obtain the Hg concentration in the effluent gas stream, as measured with the spiked trap. Compare this concentration to the corresponding Hg concentration measured with the unspiked trap. If the paired trains meet the relative deviation and other applicable data validation criteria in Table 9–1, then the average of the two Hg concentrations may be used as an emissions test run value or as the reference method value for a RATA run.

8.3 Sampling. This section describes the procedures and criteria for collecting the field samples for analysis. As noted in section 8.2.6, the field recovery test samples are also collected using these procedures.

8.3.1 Pre-test leak check. Perform a leak check of the sampling system with the sorbent traps in place. For each of the paired sampling trains, draw a vacuum in the train, and adjust the vacuum to ~15″ Hg; and, using the gas flow meter, determine leak rate. The leak rate for an individual train must not exceed 4 percent of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train, then seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct.

8.3.2 Determination of Flue Gas Characteristics. Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, etc.) in order to determine ancillary requirements such as probe heating requirements (if any), initial sampling rate, moisture management, etc.

8.3.3 Sample Collection

8.3.3.1 Remove the plug from the end of each sorbent trap and store each plug in a clean sorbent trap storage container. Remove the stack or duct port cap and insert the probe(s). Secure the probe(s) and ensure that no leakage occurs between the duct and environment.

8.3.3.2 Record initial data including the sorbent trap ID, date, and the run start time.

8.3.3.3 Record the initial gas flow meter reading, stack temperature, meter temperatures (if needed), and any other appropriate information, before beginning sampling. Begin sampling and target a sampling flow rate similar to that for the field recovery test. Then, at regular intervals (≤5 minutes) during the sampling period, record the date and time, the sample flow rate, the gas meter reading, the stack temperature, the flow meter temperatures (if using a dry gas meter), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Adjust the sampling flow rate as necessary to maintain the initial sample flow rate. Ensure that the total volume sampled for each run is within 20 percent of the total volume sampled for the field recovery test.

8.3.3.4 Data Recording. Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure must be obtained for correcting sample volume to standard conditions when using a dry gas meter. At the end of the data collection period, record the final gas flow meter reading and the final values of all other essential parameters.

8.3.3.5 Post-Test Leak Check. When sampling is completed, turn off the sample pump, remove the probe(s) with sorbent traps from the port, and carefully seal the end of each sorbent trap. Perform another leak check of each sampling train with the sorbent trap in place, at the maximum vacuum reached during the sampling period. Record the leakage rates and vacuums. The leakage rate for each train must not exceed 4 percent of the average sampling rate for the data collection period. Following each leak check, carefully release the vacuum in the sample train.

8.3.3.6 Sample Recovery. Recover each sampled sorbent trap by removing it from the probe and sealing both ends. Wipe any deposited material from the outside of the sorbent trap. Place the sorbent trap into an appropriate sample storage container and store/preserve in appropriate manner (see section 8.3.3.8).

8.3.3.7 Stack Gas Moisture Determination. If the moisture basis of the measurements made with this method (dry) is different from the moisture basis of either: (1) the applicable emission limit; or (2) a Hg CEMS being evaluated for relative accuracy, you must determine the moisture content of the flue gas and correct for moisture using Method 4 in appendix A–3 to this part. If correction of the measured Hg concentrations for moisture is required, at least one Method 4 moisture determination shall be made during each test run.

8.3.3.8 Sample Handling, Preservation, Storage, and Transport. While the performance criteria of this approach provides for verification of appropriate sample handling, it is still important that the user consider, determine and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in ASTM D6911–15 ''Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis'' (incorporated by reference-see 40 CFR 60.17) shall be followed for all samples, where appropriate. To avoid Hg contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (*e.g.*, reagent, sorbent, field, etc.) is useful in verifying the absence or source of contaminant Hg.

8.3.3.9 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840–99 ''Standard Guide for Sampling Chain-of-Custody Procedures'' shall be followed for all samples (including field samples and blanks).

9.0 Quality Assurance and Quality Control

Table 9–1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from Method 30B sorbent trap measurement systems.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Gas flow meter calibration (At 3 settings or points).	Calibration factor (Y_i) at each flow rate must be within ±2% of the average value (Y).	Prior to initial use and when post-test check is not within ±5% of Y.	Recalibrate at 3 points until the acceptance criteria are met.
Gas flow meter post-test calibration check (Single-point).	Calibration factor (Y_i) must be within ±5% of the Y value from the most recent 3-point calibration.	After each field test. For mass flow meters, must be done on-site, using stack gas.	Recalibrate gas flow meter at 3 points to determine a new value of Y. For mass flow meters, must be done on-site, using stack gas. Apply the new Y value to the field test data.
Temperature sensor calibration	Absolute temperature measures by sensor within ±1.5% of a reference sensor.	Prior to initial use and before each test thereafter.	Recalibrate; sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a mercury barometer or NIST traceable barometer.	Prior to initial use and before each test thereafter.	Recalibrate; instrument may not be used until specification is met.
Pre-test leak check	≤4% of target sampling rate	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	Sample invalidated.*
Analytical matrix interference test (wet chemical analysis, only).	Establish minimum dilution (if any) needed to eliminate sorbent matrix interferences.	Prior to analyzing any field samples; repeat for each type of sorbent used.	Field sample results not validated.
Analytical bias test	Average recovery between 90% and 110% for Hg^0 and $HgCl_2$ at each of the 2 spike concentration levels.	Prior to analyzing field samples and prior to use of new sorbent media.	Field samples shall not be analyzed until the percent recovery criteria has been met.
Multipoint analyzer calibration	Each analyzer reading within ±10% of true value *and* $r^2 \geq 0.99$.	On the day of analysis, before analyzing any samples.	Recalibrate until successful.
Analysis of independent calibration standard.	Within ±10% of true value	Following daily calibration, prior to analyzing field samples.	Recalibrate and repeat independent standard analysis until successful.

TABLE 9–1—QUALITY ASSURANCE/QUALITY CONTROL CRITERIA FOR METHOD 30B—Continued

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Analysis of continuing calibration verification standard (CCVS).	Within ±10% of true value	Following daily calibration, after analyzing ≤10 field samples, and at end of each set of analyses.	Recalibrate and repeat independent standard analysis, reanalyze samples until successful, if possible; for destructive techniques, samples invalidated.
Test run total sample volume ..	Within ±20% of total volume sampled during field recovery test.	Each individual sample	Sample invalidated.
Sorbent trap section 2 breakthrough.	For compliance/emissions testing: ≤10% of section 1 Hg mass for Hg concentrations >1 µg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 µg/dscm. ≤50% of section 1 Hg mass if the stack Hg concentration is ≤30% of the Hg concentration that is equivalent to the applicable emission limit. For relative accuracy testing: ≤10% of section 1 Hg mass for Hg concentrations >1 µg/dscm;. ≤20% of section 1 Hg mass for Hg concentrations ≤1 µg/dscm and >0.5 µg/dscm;. ≤50% of section 1 Hg mass for Hg concentrations ≤0.5 µg/dscm >0.1 µg/dscm;. no criterion for Hg concentrations ≤0.1 µg/dscm (must meet all other QA/QC specifications).	Every sample	Sample invalidated.*
Paired sorbent trap agreement	≤10% Relative Deviation (RD) mass for Hg concentrations >1 µg/dscm; ≤20% RD or ≤0.2 µg/dscm absolute difference for Hg concentrations ≤1 µg/dscm.	Every run	Run invalidated.*
Sample analysis	Within valid calibration range (within calibration curve).	All Section 1 samples where stack Hg concentration is ≥0.02 µg/dscm except in case where stack Hg concentration is ≤30% of the applicable emission limit.	Reanalyze at more concentrated level if possible, samples invalidated if not within calibrated range.
Sample analysis	Within bounds of Hg^0 and $HgCl_2$ Analytical Bias Test.	All Section 1 samples where stack Hg concentration is ≥0.5 µg/dscm.	Expand bounds of Hg^0 and $HgCl_2$ Analytical Bias Test; if not successful, samples invalidated.
Field recovery test	Average recovery between 85% and 115% for Hg^0.	Once per field test	Field sample runs not validated without successful field recovery test.

* And data from the pair of sorbent traps are also invalidated.

10.0 Calibration and Standardization

10.1 Only NIST-certified and NIST-traceable calibration standards (i.e., calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this method.

10.2 Gas Flow Meter Calibration.

10.2.1 Preliminaries. The manufacturer or equipment supplier of the gas flow meter should perform all necessary set-up, testing, programming, etc., and should provide the end user with any necessary instructions, to ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for this method.

10.2.2 Initial Calibration. Prior to its initial use, a calibration of the gas flow meter shall be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flow meter is volumetric in nature (*e.g.*, a dry gas meter), the manufacturer or end user may perform a direct volumetric calibration using any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using either: (1) A bottled gas mixture containing 12 ±0.5% CO_2, 7 ±0.5% O_2, and balance N_2 (when this method is applied to coal-fired boilers); (2) a bottled gas mixture containing CO_2, O_2, and N_2 in proportions representative of the expected stack gas composition; or (3) the actual stack gas.

10.2.2.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sampling system will be operated. You may either follow the procedures in section 10.3.1 of Method 5 in appendix A–3 to this part or in section 16 of Method 5 in appendix A–3 to this part. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

10.2.2.2 Alternative Initial Calibration Procedures. Alternatively, you may perform the initial calibration of the gas flow meter using a reference gas flow meter (RGFM). The RGFM may be: (1) A wet test meter calibrated according to section 10.3.1 of Method 5 in appendix A–3 to this part; (2) a gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of Method 5 in appendix A–3 to this part; or (3) a NIST-traceable calibration device capable of measuring volumetric flow to an accuracy of 1 percent. To calibrate the gas flow meter using the RGFM, proceed as follows: While the Method 30B sampling system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the gas flow meter being tested and the RGFM. Concurrently measure dry stack gas volume with the RGFM and the flow meter being calibrated for at least 10 minutes at each of three flow rates covering the typical range of operation of the sampling system. For each set of concurrent measurements, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

10.2.2.3 Initial Calibration Factor. Calculate an individual calibration factor Y_i at each tested flow rate from section 10.2.2.1 or 10.2.2.2 of this method (as applicable) by taking the ratio of the reference sample volume to the sample volume recorded by the gas flow meter. Average the three Y_i values, to determine Y, the calibration factor for the flow meter. Each of the three individual values of Y_i must be within ±0.02 of Y. Except as otherwise provided in sections 10.2.2.4 and 10.2.2.5 of this method, use the average Y value from the initial 3-point calibration to adjust subsequent gas volume measurements made with the gas flow meter.

10.2.2.4 Pretest On-Site Calibration Check (Optional). For a mass flow meter, if the most recent 3-point calibration of the flow meter was performed using a compressed gas mixture, you may want to conduct the following on-site calibration check prior to testing, to ensure that the flow meter will accurately measure the volume of the stack gas: While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate setting representative of normal operation of the sampling system. If the pretest calibration check shows that the value of Y_i, the calibration factor at the tested flow rate, differs from the current value of Y by more than 5 percent, perform a full 3-point recalibration of the meter using stack gas to determine a new value of Y, and (except as otherwise provided in section 10.2.2.5 of this method) apply the new Y value to the data recorded during the field test.

10.2.2.5 Post-Test Calibration Check. Check the calibration of the gas flow meter following each field test at one intermediate flow rate setting, either at, or in close proximity to, the average sample flow rate during the field test. For dry gas meters, ensure at least three revolutions of the meter during the calibration check. For mass flow meters, this check must be performed before leaving the test site, while sampling stack gas. If a one-point calibration check shows that the value of Y_i at the tested flow rate differs by more than 5 percent from the current value of Y, repeat the full 3-point calibration procedure to determine a new value of Y, and apply the new Y value to the gas volume measurements made with the gas flow meter during the field test that was just completed. For mass flow meters, perform the 3-point recalibration while sampling stack gas.

10.3 Thermocouples and Other Temperature Sensors. Use the procedures and criteria in Section 10.3 of Method 2 in appendix A–1 to this part to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against mercury-in-glass thermometers or equivalent. Calibrations must be performed prior to initial use and before each field test thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within ±1.5 percent of the temperature measured with the reference sensor, otherwise the sensor may not continue to be used.

10.4 Barometer. Calibrate against a mercury barometer or other NIST-traceable barometer as per Section 10.6 of Method 5 in appendix A–3 to this part. Calibration must be performed prior to initial use and before each test program, and the absolute pressure measured by the barometer must agree to within ±10 mm Hg of the pressure measured by the mercury or other NIST-traceable barometer, otherwise the barometer may not continue to be used.

10.5 Other Sensors and Gauges. Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

10.6 Analytical System Calibration. See section 11.1 of this method.

11.0 Analytical Procedures

The analysis of Hg in the field and quality control samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in this method. Because multiple analytical approaches, equipment and techniques are appropriate for the analysis of sorbent traps, it is not possible to provide detailed, technique-specific analytical procedures. As they become available, detailed procedures for a variety of candidate analytical approaches will be posted at *http://www.epa.gov/ttn/emc.*

11.1 Analytical System Calibration. Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges shall be calibrated, if necessary). The field samples analyzed must fall within a calibrated, quantitative range and meet the performance criteria specified below. For samples suitable for aliquotting, a series of dilutions may be needed to ensure that the samples fall within a calibrated range. However, for sorbent media samples consumed during analysis (e.g., when using thermal desorption techniques), extra care must be taken to ensure that the analytical system is appropriately calibrated prior to sample analysis. The calibration curve range(s) should be determined such that the levels of Hg mass expected to be collected and measured will fall within the calibrated range. The calibration curve may be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the square of the linear correlation coefficient, i.e., r^2, must be ≥0.99, and the analyzer response must be within ±10 percent of the reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independent standard shall be analyzed. The measured value of the independently prepared standard must be within ±10 percent of the expected value.

11.2 Sample Preparation. Carefully separate the sections of each sorbent trap. Combine for analysis all materials associated with each section; any supporting substrate that the sample gas passes through prior to entering a media section (e.g., glass wool separators, acid gas traps, etc.) must be analyzed with that segment.

11.3 Field Sample Analyses. Analyze the sorbent trap samples following the same procedures that were used for conducting the Hg^0 and $HgCl_2$ analytical bias tests. The individual sections of the sorbent trap and their respective components must be analyzed separately (*i.e.*, section 1 and its components, then section 2 and its components). All sorbent trap section 1 sample analyses must be within the calibrated range of the analytical system as specified in Table 9–1. For wet analyses, the sample can simply be diluted to fall within the calibrated range. However, for the destructive thermal analyses, samples that are not within the calibrated range cannot be re-analyzed. As a result, the sample cannot be validated, and another sample must be collected. It is strongly suggested that the analytical system be calibrated over multiple ranges so that thermally analyzed samples fall within the calibrated range. The total mass of Hg measured in each sorbent trap section 1 must also fall within the lower and upper mass limits established during the initial Hg^0 and $HgCl_2$ analytical bias test. If a sample is analyzed and found to fall outside of these limits, it is acceptable for an additional Hg^0 and $HgCl_2$ analytical bias test to be performed that now includes this level. However, some samples (e.g., the mass collected in trap section 2), may have Hg levels so low that it may not be possible to quantify them in the analytical system's calibrated range. Because a reliable estimate of these low-level Hg measurements is necessary to fully validate the emissions data, the MDL (see section 8.2.2.1 of this method) is used to establish the minimum amount that can be detected and reported. If the measured mass or concentration is below the lowest point in the calibration curve and above the MDL, the analyst must estimate the mass or concentration of the sample based on the analytical instrument response relative to an additional calibration standard at a concentration or mass between the MDL and the lowest point in the calibration curve. This is accomplished by establishing a response factor (e.g., area counts per Hg mass or concentration) and estimating the amount of Hg present in the sample based on the analytical response and this response factor.

Example: The analysis of a particular sample results in a measured mass above the MDL, but below the lowest point in the calibration curve which is 10 ng. An MDL of 1.3 ng Hg has been established by the MDL study. A calibration standard containing 5 ng of Hg is analyzed and gives an analytical response of 6,170 area counts, which equates to a response factor of 1,234 area counts/ng Hg. The analytical response for the sample is 4,840 area counts. Dividing the analytical response for the sample (4,840 area counts) by the response factor gives 3.9 ng Hg, which is the estimated mass of Hg in the sample.

11.4 Analysis of Continuing Calibration Verification Standard (CCVS). After no more than 10 samples and at the end of each set of analyses, a continuing calibration verification standard must be analyzed. The measured value of the continuing calibration standard must be within ±10 percent of the expected value.

11.5 Blanks. The analysis of blanks is optional. The analysis of blanks is useful to verify the absence of, or an acceptable level of, Hg contamination. Blank levels should be considered when quantifying low Hg levels and their potential contribution to meeting the sorbent trap section 2 breakthrough requirements; however, correcting sorbent trap results for blank levels is prohibited.

12.0 Calculations and Data Analysis

You must follow the procedures for calculation and data analysis listed in this section.

12.1 Nomenclature. The terms used in the equations are defined as follows:

B = Breakthrough (%).

B_{ws} = Moisture content of sample gas as measured by Method 4, percent/100.

C_a = Concentration of Hg for the sample collection period, for sorbent trap “a” (μg/dscm).

C_b = Concentration of Hg for the sample collection period, for sorbent trap “b” (μg/dscm).

C_d = Hg concentration, dry basis (μg/dscm).

C_{rec} = Concentration of spiked compound measured (μg/m^3).

C_w = Hg concentration, wet basis (μg/m^3).

m_1 = Mass of Hg measured on sorbent trap section 1 (μg).

m_2 = Mass of Hg measured on sorbent trap section 2 (μg).

$m_{recovered}$ = Mass of spiked Hg recovered in Analytical Bias or Field Recovery Test (μg).

m_s = Total mass of Hg measured on spiked trap in Field Recovery Test (μg).

m_{spiked} = Mass of Hg spiked in Analytical Bias or Field Recovery Test (μg).

m_u = Total mass of Hg measured on unspiked trap in Field Recovery Test (μg).

R = Percentage of spiked mass recovered (%).

RD = Relative deviation between the Hg concentrations from traps “a” and “b” (%).

v_s = Volume of gas sampled, spiked trap in Field Recovery Test (dscm).

V_t = Total volume of dry gas metered during the collection period (dscm); for the purposes of this method, standard temperature and pressure are defined as 20 °C and 760 mm Hg, respectively.

v_u = Volume of gas sampled, unspiked trap in Field Recovery Test (dscm).

12.2 Calculation of Spike Recovery (Analytical Bias Test). Calculate the percent recovery of Hg^0 and $HgCl_2$ using Equation 30B–1.

$$R = \frac{m_{recovered}}{m_{spiked}} \times 100 \qquad \text{Eq. 30B-1}$$

12.3 Calculation of Breakthrough. Use Equation 30B–2 to calculate the percent breakthrough to the second section of the sorbent trap.

$$B = \frac{m_2}{m_1} \times 100 \qquad \text{Eq. 30B-2}$$

12.4 Calculation of Hg Concentration. Calculate the Hg concentration measured with sorbent trap “a”, using Equation 30B–3.

$$C_a = \frac{(m_1 + m_2)}{V_t} \qquad \text{Eq. 30B-3}$$

For sorbent trap “b”, replace “C_a ” with “C_b ” in Equation 30B–3. Report the average concentration, i.e., ½ (C_a + C_b).

12.5 Moisture Correction. Use Equation 30B–4 if your measurements need to be corrected to a wet basis.

$$C_w = C_d \times (1 - B_{ws}) \qquad \text{Eq. 30B-4}$$

12.6 Calculation of Paired Trap Agreement. Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps using Equation 30B–5.

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \qquad \text{Eq. 30B-5}$$

12.7 Calculation of Measured Spike Hg Concentration (Field Recovery Test). Calculate the measured spike concentration using Equation 30B–6.

$$C_{rec} = \frac{m_s}{v_s} - \frac{m_u}{v_u} \qquad \text{Eq. 30B-6}$$

Then calculate the spiked Hg recovery, R, using Equation 30B–7.