

CHAPTER I -- ENVIRONMENTAL PROTECTION AGENCY  
SUBCHAPTER C -- AIR PROGRAMS

PART 60 -- STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

§ 60. Appendix A to Part 60 – Test Methods [Continued]

**40 CFR 60. Appendix A** to Part 60

METHOD 15A -- DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM SULFUR RECOVERY PLANTS IN PETROLEUM REFINERIES

*1. Applicability, Principle, Interferences, Precision, and Bias*

1.1 Applicability. This method is applicable to the determination of total reduced sulfur (TRS) emissions from sulfur recovery plants where the emissions are in a reducing atmosphere, such as in Stretford units. The lower detectable limit is 0.1 ppm of sulfur dioxide (SO<sub>2</sub>) when sampling at 2 liters/min for 3 hours or 0.3 ppm when sampling at 2 liters/min for 1 hour. The upper concentration limit of the method exceeds TRS levels generally encountered in sulfur recovery plants.

1.2 Principle. An integrated gas sample is extracted from the stack, and combustion air is added to the oxygen (O<sub>2</sub>)-deficient gas at a known rate. The TRS compounds (hydrogen sulfide, carbonyl sulfide, and carbon disulfide) are thermally oxidized to sulfur dioxide, collected in hydrogen peroxide as sulfate ion, and then analyzed according to the Method 6 barium-thorin titration procedure.

1.3 Interferences. Reduced sulfur compounds, other than TRS, that are present in the emissions will also be oxidized to SO<sub>2</sub>. For example, thiophene has been identified in emissions from a Stretford unit and produced a positive bias of 30 percent in the Method 15A result. However, these biases may not affect the outcome of the test at units where emissions are low relative to the standard.

Calcium and aluminum have been shown to interfere in the Method 6 titration procedure. Since these metals have been identified in particulate matter emissions from Stretford units, a Teflon filter is required to remove this interference.

NOTE: Mention of trade name or commercial products in this publication does not constitute the endorsement or recommendation for use by the Environmental Protection Agency.

When used to sample emissions containing 7 percent moisture or less, the midget impingers have sufficient volume to contain the condensate collected during sampling. Dilution of the H<sub>2</sub>O does not affect the collection of SO<sub>2</sub>. At higher moisture contents, the potassium citrate-citric acid buffer system used with Method 16A should be used to collect the condensate.

1.4 Precision and bias. Relative standard deviations of 2.8 and 6.9 percent at 41 ppm TRS have been obtained when sampling for 1 and 3 hours, respectively. Results obtained with this method are likely to contain a positive bias due to the presence of nonregulated sulfur compounds (that are present in petroleum) in the emissions.

*2. Apparatus*

2.1 Sampling. The sampling train is shown in Figure 15A-1, and component parts are discussed below.

Modifications to this sampling train are acceptable provided that the system performance check is met.

Figure 15A-1. Method 15A sampling train.

[SEE FIGURE IN ORIGINAL]

2.1.1 Probe. 0.6-cm (1/4-in.) OD Teflon tubing sequentially wrapped with heat-resistant fiber strips, a rubberized heating tape (with a plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or some other suitable temperature-measuring device shall be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored. 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 flue gas from entering between the probe and sheath. The sampling probe is depicted in Figure 15A-2.

Figure 15A-2. Method 15A sampling probe.

[SEE FIGURE IN ORIGINAL]

2.1.2 Particulate filter. A 50-mm Teflon filter holder and a 1- to 2-  $\mu$ m porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55345). The filter holder must be maintained in a hot box at a high enough temperature to prevent condensation.

2.1.3 Combustion air delivery system. As shown in the schematic diagram in Figure 15A-3. The rotameter should be selected to measure an air flow rate of 0.5 liter/min.

Figure 15A-3. Combustion air delivery system.

[SEE FIGURE IN ORIGINAL]

2.1.4 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 at 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.

2.1.5 Furnace. Of sufficient size to enclose the combustion tube. The furnace shall have a temperature regulator capable of maintaining the temperature at 1100  $\pm$  50 deg. C. The furnace operating temperature shall be checked with a thermocouple to ensure accuracy. Lindberg furnaces have been found to be satisfactory.

2.1.6 Peroxide impingers, stopcock grease, thermometer, drying tube, valve, pump, barometer, and vacuum gauge. Same as in Method 6, Sections 2.1.2, 2.1.4, 2.1.5, 2.1.6, 2.1.7, 2.1.8, 2.1.11, and 2.1.12, respectively.

2.1.7 Rate meters. Rotameters (or equivalent) capable of measuring flow rate to within 5 percent of the selected flow rate and calibrated as in Section 5.2.

2.1.8 Volume meter. Dry gas meter capable of measuring the sample volume under the particular sampling conditions with an accuracy of  $\pm$  2 percent.

2.1.9 U-tube manometer. To measure the pressure at the exit of the combustion gas dry gas meter.

2.2 Sample recovery and analysis. Same as in Method 6, Sections 2.2 and 2.3, except a 10-ml buret with 0.05-ml graduations is required for titrant volumes of less than 10.0 ml, and the spectrophotometer is not needed.

### 3. Reagents

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 shall be used.

3.1 Sampling. The following reagents are needed:

3.1.1 Water. Same as in Method 6, Section 3.1.1.

3.1.2 Hydrogen peroxide, 3 percent. Same as in Method 6, Section 3.1.5 (40 ml is needed per sample).

3.1.3 Recovery check gas. Carbonyl sulfide (COS) in nitrogen (100 ppm or greater, if necessary) in an aluminum cylinder. Verify the concentration by gas chromatography where the instrument is calibrated with a COS permeation tube.

3.1.4 Combustion gas. Air, contained in a gas cylinder equipped with a two-stage regulator. The gas should contain less than 50 ppb of reduced sulfur compounds and less than 10 ppm total hydrocarbons.

3.2 Sample recovery and analysis. Same as in Method 6, Sections 3.2 and 3.3.

### 4. Procedure

4.1 Sampling. Before any source sampling is done, conduct two 30-minute system performance checks in the field, as detailed in Section 4.3, to validate the sampling train components and procedures (optional).

4.1.1 Preparation of sampling train. For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midjet impingers. Leave the third midjet impinger empty and add silica gel to the fourth impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Place crushed ice and water around all impingers. Maintain the oxidation furnace at 1100 +/- 50 deg. C to ensure 100 percent oxidation of COS. Maintain the probe and filter temperatures at a high enough level (no visible condensation) to prevent moisture condensation and monitor the temperatures with a thermocouple.

4.1.2 Leak-check procedure. Assemble the sampling train and leak-check as described in Method 6, Section 4.1.2. Include the combustion air delivery system from the needle valve forward in the leak-check.

4.1.3 Sample collection. Adjust the pressure on the second stage of the regulator on the combustion air cylinder to 10 psig. Adjust the combustion air flow rate to 0.50 liter/min (+/- 10 percent) before injecting combustion air into the sampling train. Then inject combustion air into the sampling train, start the sample pump, and open the stack sample gas valve. Carry out these three operations within 15 to 30 seconds to avoid pressurizing the sampling train. Adjust the total sample flow rate to 2.0 liters/min (+/- 10 percent). The combustion air flow rate of 0.50 liter/min and the total sample flow rate of 2.0 liters/min produce an O<sub>2</sub> concentration of 5.0 percent in the stack gas. This O<sub>2</sub> concentration must be maintained constantly to allow oxidation of TRS to SO<sub>2</sub>. Adjust these flow rates during sampling as necessary. Monitor and record the combustion air manometer reading at regular intervals during the sampling period. Sample for 1 or 3 hours. At the end of sampling, turn off the sample pump and combustion air simultaneously (within 15 to 30 seconds of each other). All other procedures are the same as in Method 6, Section 4.1.3, except that the sampling train should not be purged. After collecting the sample, remove the probe from the stack and conduct a leak-check (mandatory).

After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see Section 4.3). After this system performance check and before the next test run, it is recommended that the probe be rinsed and brushed and the filter replaced.

In Method 15, 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 15A to be consistent with Method 15, 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.)

4.2 Sample recovery. Recover the hydrogen peroxide-containing impingers as detailed in Method 6, Section 4.2.

4.3 System performance check. A system performance check is done (1) to validate the sampling train components and procedure (before testing, optional) and (2) to validate a test run (after a run). Perform a check in the field before 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).

The checks involve sampling a known concentration of COS and comparing the analyzed concentration with the known concentration. Mix the recovery gas with N<sub>2</sub> as shown in Figure 15A-4 if dilution is required. Adjust the flow rates to generate a COS concentration in the range of the stack gas or within 20 percent of the applicable standard at a total flow rate of at least 2.5 liters/min. Use Equation 15A-4 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow tube so that the diluted concentration of COS can be accurately calculated. Collect 30-minute samples, and analyze in the normal manner. Collect the samples through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

[SEE FIGURE IN ORIGINAL]

Figure 15A-4. COS recovery gas generator system.

The recovery check must be performed in the field before replacing the particulate filter and before cleaning the probe. A sample recovery of 100 +/- 20 percent must be obtained for the data to be valid and should be reported with the emission data, but should not be used to correct the data. However, if the performance check 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. Use Equation 15A-5 to calculate the recovery efficiency.

4.4 Sample analysis. Same as in Method 6, Section 4.3. For compliance tests only, an EPA SO<sub>2</sub> field audit sample shall be analyzed with each set of samples. Such audit samples are available from the Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

## 5. Calibration.

5.1 Metering system, thermometers, barometer, and barium perchlorate solution. Calibration procedures are presented in Method 6, Sections 5.1, 5.2, 5.4, and 5.5.

5.2 Rotameters. Calibrate with a bubble flow tube.

## 6. Calculations.

In the calculations, retain at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

### 6.1 Nomenclature.

C[TRS] = Concentration of TRS as SO<sub>2</sub>, dry basis, corrected to standard conditions, ppm.

N = Normality of barium perchlorate titrant, milliequivalents/ml.

P[bar] = Barometric pressure at exit orifice of the dry gas meter, mm Hg.

P[std] = Standard absolute pressure, 760 mm Hg.

T[m] = Average dry gas meter absolute temperature, deg.

T[std] = Standard absolute temperature, 293 deg.

V[a] = Volume of sample aliquot titrated, ml.

V[ms] = Dry gas volume as measured by the sample train dry gas meter, liters.

V[mc] = Dry gas volume as measured by the combustion air dry gas meter, liters.

V[ms(std)] = Dry gas volume measured by the sample train dry gas meter, corrected to standard conditions, liters.

V[mc(std)] = Dry gas volume measured by the combustion air dry gas meter, corrected to standard conditions, liters.

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 (average of replicate titrations), ml.

V[tb] = Volume of barium perchlorate titrant used for the blank, ml.

Y = Calibration factor for sampling train dry gas meter.

Y[c] = Calibration factor for combustion air dry gas meter.

C[RG] = Concentration of generated recovery gas, ppm.

C[CO<sub>S</sub>] = Concentration of CO<sub>S</sub> recovery gas, ppm.

Q[CO<sub>S</sub>] = Flow rate of CO<sub>S</sub> recovery gas, liters/min.

Q[N<sub>2</sub>] = Flow rate of diluent N<sub>2</sub>, liters/min.

R = Recovery efficiency for the system performance check, percent.

32.03 = Equivalent weight of sulfur dioxide, mg/meq.

$12025 \mu\text{l} / \text{meq} = ((32.03 \text{ mg}) / (\text{meq})) \times ((24.05 \text{ liters}) / (\text{mole})) \times ((\text{mole}) \times (1 \text{ g}) \times (10^3 \text{ ml}) \times (10^3 \mu\text{l})) / (64.06 \text{ g}) \times (10^3 \text{ g}) \times (\text{liter}) \times (\text{ml})$

6.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$V[\text{ms}(\text{std})] = ((V[\text{ms}] \times Y \times (T[\text{std}]) \times (P[\text{bar}]))) / (T[\text{m}] \times (P[\text{std}])) = (K[1] \times Y \times (V[\text{m}] \times (P[\text{bar}])) / T[\text{m}]$

Eq. 15A-1

where:  $K[1] = 0.3858 \text{ deg. K/mm Hg}$  for metric units.

6.3 Combustion Air Gas Volume, Corrected to Standard Conditions.

$$V[\text{mc}(\text{std})] = (k[1] \times Y[\text{c}] \times (V[\text{mc}]) \times (P[\text{bar}])) / T[\text{m}]$$

Eq. 15A-2

NOTE: Correct  $P[\text{bar}]$  for the average pressure of the manometer during the sampling period.

6.4 Concentration of TRS as ppm  $\text{SO}_2$ .

$$C[\text{TRS}] = (K[2] \times (V[\text{t}] - V[\text{tb}]) \times N \times (V[\text{soln}] / V[\text{a}])) / (V[\text{ms}(\text{std})] - V[\text{mc}(\text{std})])$$

Eq. 15A-3

where:  $K[2] = 12025 \text{ } \mu\text{l/meq}$  for metric units.

6.5 Concentration of Generated Recovery Gas.

$$C[\text{RG}] = ((C[\text{COS}]) (Q[\text{COS}])) / (Q[\text{COS}] + Q[\text{N}_2])$$

Eq. 15A-4

6.6 Recovery Efficiency.

$$R = (C[\text{TRS}] / C[\text{RG}]) \times 100$$

Eq. 15A-5

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## METHOD 16 -- SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

### *Introduction*

The method described below uses the principle of gas chromatographic 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. *Principle and Applicability*

1.1 Principle. A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H<sub>2</sub>S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are known collectively as total reduced sulfur (TRS).

1.2 Applicability. This method is applicable for determination of TRS compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills.

### 2. *Range and Sensitivity*

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

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

### 3. *Interferences*

3.1 Moisture Condensation. 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 deg. C (248 deg. F). Moisture is removed in the SO<sub>2</sub> scrubber and heating the sample beyond this point is not necessary provided the ambient temperature is above 0 deg. C. 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.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO<sub>2</sub> 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<sub>2</sub> in the diluent gas. The CO<sub>2</sub> level should be approximately 10 percent for the case with CO<sub>2</sub> present. The two chromatograms should show agreement within the precision limits of Section 4.1.

3.3 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.

3.4 Sulfur Dioxide (SO<sub>2</sub>). Sulfur dioxide is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO<sub>2</sub> scrubber described in Section 5.1.3 will effectively remove SO<sub>2</sub> from the sample.

#### 4. *Precision and Accuracy*

4.1 GC/FPD Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than +/- 5 percent from the mean of the three injections.

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

4.3 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.

#### 5. *Apparatus*

##### 5.1. Sampling.

##### 5.1.1 Probe.

Figure 16-1. Probe used for sample gas containing high particulate loadings.

[SEE FIGURE IN ORIGINAL]

5.1.1.1 Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It shall 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.

5.1.1.2 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 2.1.1 of Methods 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

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

5.1.2 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 deg. C (248 deg. F).

##### 5.1.3 SO<sub>2</sub> Scrubber.



5.1.3.1 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 deg. C. 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.

5.1.3.2 Connections between the probe, particulate filter, and SO<sub>2</sub> scrubber shall be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO<sub>2</sub> scrubber (or alternative point of moisture removal) shall be maintained at a temperature of at least 120 deg. C (248 deg. F).

5.1.4 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.

5.1.5 Sample Pump. The sample pump shall be leakless Teflon-coated diaphragm type or equivalent.

5.2 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.

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

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature +/- 1 deg. C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature +/- 1 deg. C.

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

5.3.4 Flame Photometric Detector.

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

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

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

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

5.4 Gas Chromatogram Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H<sub>2</sub>S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences.

To demonstrate that adequate resolution has been achieved, the tester must 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.

5.5 Calibration System. The calibration system must contain the following components. (Figure 16-2)

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

5.5.2 Flow System. To measure air flow over permeation tubes at +/- 2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lower flow measurement. Calibration with a wet test meter before a test is optional. Flow over the permeation device may also be determined using a soap bubble flowmeter.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within +/- 0.1 deg. C.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within +/- 1 deg. C.

## 6. Reagents

6.1 Fuel. Hydrogen (H<sub>2</sub>), prepurified grade or better.

6.2 Combustion Gas. Oxygen (O<sub>2</sub>) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent (If required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

6.5 Calibration Gases. Permeation tubes, one each of H<sub>2</sub>S, 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.

6.6 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. 284 grams of sodium citrate may be substituted for the potassium citrate. Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

6.7 Sample Line Loss Gas (Optional). As an alternative to permeation gas, H<sub>2</sub>S cylinder gas may be used for the sample line loss test. The gas shall be calibrated against permeation devices having known permeation rates or by the procedure in Section 7 of Method 16A.

## 7. Pretest Procedures

The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

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

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: 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 greater than 50 mm (2 in.) Hg vacuum, 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. As an alternative to the initial leak-test, the sample line loss test described in Section 10.1 may be performed to verify the integrity of components.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. In any component, or if the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

## 8. Calibration

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in Section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system (if applicable). The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components, particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within +/- 0.1 deg. C. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of Section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K P[r] / ML$$

Eq. 16-1

Where:

C = Concentration of permeant produced in ppm.

P[r] = Permeation rate of the tube in  $\mu\text{g}/\text{min}$ .

M = Molecular weight of the permeant (g/g-mole).

L = Flow rate, l/min, of air over permeant at 20 deg. C, 760 mm Hg.

K = Gas constant at 20 deg. C and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of Analysis System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.5 to 10 ppm for a 1-ml sample) for each of the four major sulfur compounds. Inject these standards into the GC/FPD analyzer and monitor the responses. Three injects for each concentration must not vary by more than 5 percent from the mean of the three injections. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data. Alternatively, a least squares equation may be generated from the calibration data using concentrations versus the appropriate instrument response units.

## 9. *Sampling and Analysis Procedure*

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe or Filter. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe or filter is clogged with particulate matter. If either is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning or replacing the probe and filter. After each run, the probe and filter shall be inspected and, if necessary, replaced.

## 10. *Post-Test Procedures*

10.1 Sample line loss. A known concentration of hydrogen sulfide at the level of the applicable standard, +/- 20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. (See figure 16-1). The resulting measured concentration should be compared to the known value to determine the sampling system loss.

For sampling losses greater than 20 percent in a sample run, the sample run is not to be used when determining the arithmetic mean of the performance test. For sampling losses of 0-20 percent, the sample concentration must be corrected by dividing the sample concentration by the fraction of recovery. The fraction of recovery is equal to one minus the ratio of the measured concentration to the known concentration of hydrogen sulfide in the sample line loss procedure. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in nitrogen and certified according to section 6.7 may be used. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

Figure 16-2. Determination of sample line loss.

[SEE FIGURE IN ORIGINAL]

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 8. Only H<sub>2</sub>S (or other calibration gas) need be used to recalibrate the GC/FPD analysis system (Section 8.3).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under Section 10.2. The calibration drift should not exceed the limits set forth in Section 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

### 11. Calculations

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least squares line.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$\text{TRS} = \text{SIGMA} (\text{H}_2\text{S}, \text{MeSH}, \text{DMS}, 2\text{DMDS})d$$

Eq. 16-2

Where:

TRS = Total reduced sulfur in ppm, dry basis.

H<sub>2</sub>S = Hydrogen sulfide, ppm.

MeSH = Methyl mercaptan, ppm.

DMS = Dimethyl sulfide, ppm.

DMDS = Dimethyl disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Average TRS} = \langle n \rangle \text{SIGMA} [i = 1] \text{TRS}[1] / N(1 - B[\text{wo}])$$

Where:

Average TRS = Average total reduced sulfur in ppm, dry basis.

TRS[1] = 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 reference Method 4 -- Determination of Moisture in Stack Gases.

#### 11.4 Average Concentration of Individual Reduced Sulfur Compounds.

$$C = \langle n \rangle \text{SIGMA } [i = 1] S[i] / N$$

Eq. 16-4

Where:

S[i] = Concentration of any reduced sulfur compound from the ith 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.

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

#### 1. *Applicability, Principle, Interferences, Precision, and Bias*

1.1 *Applicability*. This method is applicable to the determination of total reduced sulfur (TRS) emissions from recovery 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 TRS compounds include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to sulfur dioxide (SO<sub>2</sub>).

The lower detectable limit is 0.1 ppm SO<sub>2</sub> when sampling at 2 liters/min for 3 hours or 0.3 ppm when sampling at 2 liters/min for 1 hour. The upper concentration limit of the method exceeds TRS levels generally encountered at kraft pulp mills.

1.2 Principle. An integrated gas sample is extracted from the stack. SO<sub>2</sub> is removed selectively from the sample using a citrate buffer solution. TRS compounds are then thermally oxidized to SO<sub>2</sub>, collected in hydrogen peroxide as sulfate, and analyzed by the Method 6 barium-thorin titration procedure.

1.3 Interferences. TRS 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<sub>2</sub> and may be present in a lime kiln exit stack, would be a positive interferent.

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<sub>2</sub>S 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 2.1.3 will eliminate this interference.

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

In a separate study at a recovery boiler, Method 16A was found to be unbiased relative to Method 16. 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.

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

## 2. Apparatus

2.1 Sampling. 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 (Section 4.3) is met.

### Figure 16A-1. Sampling Train

[SEE FIGURE IN ORIGINAL]

2.1.1 Probe. Teflon (mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency) tubing, 0.6-cm (1/4-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 0.6-cm (1/4-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 sampling probe is depicted in Figure 16A-2.

### Figure 16A-2. Angled sampling probe

[SEE FIGURE IN ORIGINAL]

2.1.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm (1/8-in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

2.1.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-  $\mu$  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 deg. C (250 deg. F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

2.1.4 SO<sub>2</sub> 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.).

2.1.5 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 (1/4 in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector at 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.

2.1.6 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  $\pm$  100 deg. C. The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

2.1.7 Peroxide Impingers, Stopcock Grease, Thermometer, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge. Same as in Method 6, Sections 2.1.2, 2.1.4, 2.1.6, 2.1.7, 2.1.8, 2.1.11, and 2.1.12, respectively.

2.1.8 Rate Meter. Rotameter, or equivalent, accurate to within 5 percent at the selected flow rate of 2 liters/min.

2.1.9 Volume Meter. Dry gas meter capable of measuring the sample volume under the sampling conditions of 2 liters/min with an accuracy of  $\pm$  2 percent.

2.1.10 Polyethylene Bottles. 250-ml bottles for hydrogen peroxide solution recovery.

2.2 Sample Preparation and Analysis. Same as in Method 6, Section 2.3, except a 10-ml buret with 0.05-ml graduations is required and the spectrophotometer is not needed.

### 3. Reagents

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 shall be used.

3.1 Sampling. The following reagents are needed:

3.1.1 Water. Same as in Method 6, Section 3.1.1.

3.1.2 Citrate Buffer. 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid dissolved 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.

3.1.3 Hydrogen Peroxide, 3 percent. Same as in Method 6, Section 3.1.3 (40 ml is needed per sample).



3.1.4 Recovery Check Gas. Hydrogen sulfide (100 ppm 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<sub>2</sub>S permeation tube as described below. For Method 11, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

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, an H<sub>2</sub>S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

3.1.5 Combustion Gas. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppm 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.

3.2 Sample Recovery and Analysis. Same as in Method 6, Sections 3.2.1 and 3.3.

#### 4. Procedure

4.1 Sampling. Before any source sampling is done, conduct two 30-minute system performance checks in the field as detailed in Section 4.3 to validate the sampling train components and procedure (optional).

4.1.1 Preparation of Collection Train. For the SO<sub>2</sub> 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 indicator.

For the Method 6 part of the train, measure 20 ml of 3 percent hydrogen peroxide into the first and second midjet impingers. Leave the third midjet impinger empty, and place silica gel in the fourth midjet impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Maintain the oxidation furnace at 800 +/- 100 deg. C. Place crushed ice and water around all impingers.

4.1.2 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 4.1.2.

4.1.3 Sample Collection. Same as in Method 6, Section 4.1.3, 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 4.1.2. 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 4.3) 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 (recommended but optional).

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.)

4.2 Sample Recovery. Disconnect the impingers. Quantitatively transfer the contents of the midjet impingers of the Method 6 part of the train into a leak-free polyethylene bottle for shipment. Rinse the three midjet 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.

4.3 System Performance Check. 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 a least two samples (optional), and perform an additional check after each 3-hour run or after three 1-hour samples (mandatory).

The checks involve sampling a known concentration of H<sub>2</sub>S and comparing the analyzed concentration with the known concentration. Mix the H<sub>2</sub>S recovery gas (Section 3.1.4) and combustion gas in a dilution system such as is shown in Figure 16A-3. Adjust the flow rates to generate an H<sub>2</sub>S 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. Use Equation 16A-3 to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow tube so that the diluted concentration of H<sub>2</sub>S can be accurately calculated. Collect 30-minute samples, and analyze in the normal manner (as discussed in Section 4.1.3). 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.

[SEE FIGURE IN ORIGINAL]

Figure 16A-3. Recovery gas dilution system.

The recovery check must be performed in the field prior to replacing the SO<sub>2</sub> scrubber and particulate filter and before the probe is cleaned. A sample recovery of 100 +/- 20 percent must be obtained for the data to be valid and should be reported with the emission data, but should not be used to correct the data. However, if the performance check 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. Use Equation 16A-4 to calculate the recovery efficiency.

4.4 Sample Analysis. Same as in Method 6, Section 4.3, except for 1-hour sampling, take a 40-ml aliquot, add 160 ml of 100 percent isopropanol, and four drops of thorin. Analyze an EPA SO<sub>2</sub> field audit sample with each set of samples. Such audit samples are available from the Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

## 5. Calibration

5.1 Metering System, Thermometers, Rotameters, Barometers, and Barium Perchlorate Solution. Calibration procedures are presented in Method 6, Sections 5.1 through 5.5.

## 6. 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.

### 6.1 Nomenclature.

C[TRS] = Concentration of TRS as SO<sub>2</sub>, dry basis corrected to standard conditions, ppm.

C[RG] = Concentration of recovery gas generated, ppm.

C[H<sub>2</sub>S] = Verified concentration of H<sub>2</sub>S 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[H<sub>2</sub>S] = Calibrated flow rate of H<sub>2</sub>S 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, deg. K (deg. R).

T[std] = Standard absolute temperature, 293 deg. K, (528 deg. 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.

6.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V[m(std)] = V[m] Y T[std] / T[m] \times P[bar] / P[std] = K[1] Y \times V[m] - P[bar] / T[m]$$

Where: K[1] = 0.3858 deg. K/mm Hg for metric units.

6.3 Concentration of TRS as ppm SO<sub>2</sub>.

$$C[TRS(ppm)] = K[2] (V[t] - V[tb]) N (V[soln] / V[a] / V[m(std)])$$

Eq. 16A-2

Where: K[2] = 32.03 X mg / meq X 24.05 liters / mole X 1 g / 1000 mg X 1000 ml/ liter X 1000 μl / 1 ml = 12025 X μl / meq

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

$$C[RG] = (Q[H_2S]) (C[H_2S]) / Q [H_2S] + Q[CG]$$

Eq. 16A-3

6.5 Recovery Efficiency for the System Performance Check.

$$R = C[TRS] / C[RG] \times 100 \text{ Eq.}$$

16A-4

## 7. Alternative Procedures

**7.1 Determination of H<sub>2</sub>S Content in Cylinder Gases.** As an alternative to the procedures specified in section 3.1.4, the following procedure may be used to verify the concentration of the recovery check gas. The H<sub>2</sub>S 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. The method has been examined in the range of 5 to 1500 ppm. There are no known interferences to this method when used to analyze cylinder gases containing H<sub>2</sub>S in nitrogen. Laboratory tests have shown a relative standard deviation of less than 3 percent. The method showed no bias when compared to a gas chromatographic method that used gravimetrically certified permeation tubes for calibration.

**7.1.1 Sampling Apparatus.** The sampling train is shown in Figure 16A-4 and consists of the following components:

[SEE FIGURE IN ORIGINAL]

Figure 16A-4. Recovery check gas sampling train.

**7.1.1.1 Sampling Line.** Teflon tubing (1/4-in.) to connect the cylinder regulator to the sampling valve.

**7.1.1.2 Needle Valve.** Stainless Steel or Teflon needle valve to control the flow rate of gases to the impingers.

**7.1.1.3 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 impingers bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 1/4-in. (0.64-cm) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1/2 in. (1.27-cm) from the bottom (Southern Scientific, Inc., Micanopy, Florida: Set Number S6962-048). The third in-line impinger acts as a drop-out bottle.

**7.1.1.4 Drying Tube, Flowmeter, and Barometer.** Same as in Method 11, Sections 5.1.5, 5.1.8, and 5.1.10.

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

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

**7.1.1.7 Critical Orifice.** For volume and rate measurements. The critical orifice may be fabricated according to Section 7.1.4.3 and must be calibrated as specified in Section 7.1.8.4.

**7.1.1.8 Graduated Cylinder.** 50-ml size.

7.1.1.9 *Volumetric Flask*. 1-liter size.

7.1.1.10 *Volumetric Pipette*. 15-ml size.

7.1.1.11 *Vacuum Gauge*. Minimum 20-in. Hg capacity.

7.1.1.12 *Stopwatch*.

7.1.2 *Sample Recovery and Analysis Apparatus*.

7.1.2.1 *Erlenmeyer Flasks*. 125- and 250-ml sizes.

7.1.2.2 *Pipettes*. 2-, 10-, 20-, and 100-ml volumetric.

7.1.2.3 *Burette*. 50-ml size.

7.1.2.4 *Volumetric Flask*. 1-liter size.

7.1.2.5 *Graduated Cylinder*. 50-ml size.

7.1.2.6 *Wash Bottle*.

7.1.2.7 *Stirring Plate and Bars*.

7.1.3 *Reagents*. Unless otherwise indicated, all reagents shall 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.

7.1.3.1 *Water*. Same as in Method 11, Section 6.1.3.

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

7.1.3.3 *Potassium Bi-iodate [KH(IO<sub>3</sub>)<sub>2</sub>] Solution, Standard 0.100 N*. Dissolve 3.249 g anhydrous KH(IO<sub>3</sub>)<sub>2</sub> in water, and dilute to 1 liter.

7.1.3.4 *Sodium Thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) Solution, Standard 0.1 N*. Same as in Method 11, Section 6.3.1. Standardize according to Section 7.1.8.2.

7.1.3.5 *Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) Solution, Standard 0.01 N*. Pipette 100.0 ml of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution into a 1-liter volumetric flask, and dilute to the mark with water.

7.1.3.6 *Iodine Solution, 0.1 N*. Same as in Method 11, Section 6.2.2.

7.1.3.7 *Standard Iodine Solution, 0.01 N*. Same as in Method 11, Section 6.2.3. Standardize according to Section 7.1.8.3.

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

7.1.3.9 *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.

#### 7.1.4 Sampling Procedure.

7.1.4.1 *Selection of Gas Sample Volumes.* This procedure has been validated for estimating the volume of cylinder gas sample needed when the H<sub>2</sub>S concentration is in the range of 5 to 1500 ppm. 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) titer of approximately 7 to 12 ml). The sample volumes for various H<sub>2</sub>S concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the H<sub>2</sub>S concentration stated by the manufacturer.

Approximate cylinder gas H <sub>2</sub> S concentration (ppm)	Approximate ppm-liters desired
5 to < 30	650
30 to < 500	800
500 to < 1500	1000

For example, for analyzing a cylinder gas containing approximately 10 ppm H<sub>2</sub>S, the optimum sample volume is 65 liters (650 ppm-liters/10 ppm). For analyzing a cylinder gas containing approximately 1000 ppm H<sub>2</sub>S, the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppm).

7.1.4.2 *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<sub>2</sub>S in the impinger solution. Slight deviations from these ranges will not have an impact on measured concentrations.

Cylinder gas H <sub>2</sub> S concentration (ppm)	Critical orifice flow rate (ml/min)
5 to < 50 ppm	1500 +/- 500
50 to < 250 ppm	500 +/- 250
250 to < 1000 ppm	200 +/- 50
> 1000 ppm	75 +/- 25

7.1.4.3 *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. X 1/4-in. (0.16-cm X 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 Length	Flow rate Altech
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	(in. ID)	(in.)	(ml/ min)	catalog No.	n1
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	

n1 Altech Associates, 2051 Waukegon Road., Deerfield, Illinois 60015.

**7.1.4.4 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<sub>2</sub>S 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 7.1.4.2, proceed with the critical orifice calibration according to Section 7.1.8.4.

**7.1.4.5 Determination of Approximate Sampling Time.** Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in Section 7.1.4.1.

Approximate sampling time (min) = Optimum volume X 1000 / Critical orifice flow rate (ml/min)

**7.1.4.6 Sample Collection.** 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.

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.

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 7.1.4.5.

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.

**7.1.5 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. 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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.

7.1.6 *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<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. 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.

7.1.7 *Post-test Orifice Calibration.* Conduct a post-test critical orifice calibration run using the calibration procedures outlined in Section 7.1.8.4. 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.

7.1.8 *Calibrations and Standardizations.*

7.1.8.1 *Rotameter and Barometer.* Same as in Method 11, Sections 8.2.3 and 8.2.4.

7.1.8.2 *Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Solution, 0.1 N.* Standardize the 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated H<sub>2</sub>SO<sub>4</sub>, 10.0 ml 0.100 N KH(IO<sub>3</sub>)<sub>2</sub> and 1 g potassium iodide. Titrate immediately with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> consumed to calculate the normality to three decimal figures using Equation 16A-5.

7.1.8.3 *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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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.

7.1.8.4 *Critical Orifice.* Calibrate the critical orifice using the sampling train shown in Figure 16A-4 but without the H<sub>2</sub>S 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 7.1.4.4. 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 1. Use these data to calculate the volumetric flow rate of the orifice.

7.1.9 *Calculations.*

7.1.9.1 *Nomenclature.*

B[wa] = Fraction of water vapor in ambient air during orifice calibration.



$C[H_2S]$  =  $H_2S$  concentration in cylinder gas, ppm.

$K$  = Conversion factor = 12025 ml/eq

= 17.03 g / g-eq X 24.05 liters  $H_2S$  / mole  $H_2S$  X 1 mole  $H_2S$  / 34.06 g  $H_2S$  X 10<sup>3</sup> ml / liter

$M[a]$  = 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. (For tests carried out in a laboratory where the impinger temperature is 25 deg. 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.

$Q[std]$  = Volumetric flow rate through critical orifice, liters/min.

Date

Critical orifice ID

Soap bubble meter volume,  $V[sb]$  liters

Time, circle minus[ab]

Run no. 1 min sec

Run no. 2 min sec

Run no. 3 min sec

Average min sec

Convert the seconds to fraction of minute:

Time

= min + Sec/60

= min

Barometric pressure,  $P[bar]$  = mm Hg

Ambient temperature,  $t[amb]$  = 273 + deg. C = deg. K

Pump vacuum, = mm Hg. (This should be approximately 0.4 times barometric pressure.)

$$V[\text{sb}(\text{std})] = (V[\text{sb}])(T[\text{std}])(P[\text{bar}])(10^{-3}) / (T[\text{amb}]) (P[\text{std}])$$

= --liters

$$Q[\text{std}] = V[\text{sb}(\text{std})] / \text{theta}[\text{sb}]$$

= --liters/min

#### TABLE 1 -- CRITICAL ORIFICE CALIBRATION DATA.

$Q[\text{std, average}]$  = Average standard flow rate through critical orifice, liters/min.

$Q[\text{std, before}]$  = Average standard flow rate through critical orifice determined before H<sub>2</sub>S sampling (Section 7.1.4.4), liters/min.

$Q[\text{std, after}]$  = Average standard flow rate through critical orifice determined after H<sub>2</sub>S sampling (Section 7.1.7), liters/min.

$T[\text{amb}]$  = Absolute ambient temperature, deg. K.

$T[\text{std}]$  = Standard absolute temperature, 293 deg. K.

$\text{Theta minus}[s]$  = Sampling time, min.

$\text{Theta minus}[sb]$  = Time for soap bubble meter flow rate measurement, min.

$V[m(\text{std})]$  = Sample gas volume measured by the critical orifice, corrected to standard conditions, liters.

$V[\text{sb}]$  = Volume of gas as measured by the soap bubble meter, ml.

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

$V[\text{I}]$  = Volume of standard iodine solution (0.01 N) used, ml.

$V[\text{T}]$  = Volume of standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.01 N) used, ml.

$V[\text{TB}]$  = Volume of standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.01 N) used for the blank, ml.

7.1.9.2 Normality of Standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Solution (0.1. N).

$N[\text{T}] = 1 / \text{ml Na}_2\text{S}_2\text{O}_3 \text{ Consumed}$

Eq. 16A-5

7.1.9.3 Normality of Standard Iodine Solution (0.01 N)

$N[\text{I}] = N[\text{T}] V[\text{T}] / V[\text{I}]$

Eq. 16A-6

7.1.9.4 Sample Gas Volume.

$$V[m(\text{std})] = (Q[\text{std}] (\text{Theta}[s]) (1 - B[\text{wa}]) X M[\text{a}] / M[\text{b}]$$

Eq. 16A-7

7.1.9.5 Concentration of H<sub>2</sub>S in the Gas Cylinder.

$$C[\text{H}_2\text{S}] = K N[\text{T}] (V[\text{TB}] - V[\text{T}]) / V[m(\text{std})]$$

Eq. 16A-8

## 8. Bibliography

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METHOD 16B -- DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM

## STATIONARY SOURCES

### 1. *Applicability, Principle, Range and Sensitivity, Interferences, and Precision and Accuracy*

1.1 *Applicability.* This method is applicable to the determination of total reduced sulfur (TRS) emissions from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The TRS compounds include hydrogen sulfide (H<sub>2</sub>S), methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to sulfur dioxide (SO<sub>2</sub>).

1.2 *Principle.* An integrated gas sample is extracted from the stack. The SO<sub>2</sub> is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO<sub>2</sub> and analyzed as SO<sub>2</sub> by gas chromatography (GC) using flame photometric detection (FPD).

1.3 *Range and Sensitivity.* Coupled with a GC utilizing a 1-ml sample size, the maximum limit of the FPD for SO<sub>2</sub> is approximately 10 ppm. This limit is expanded by dilution of 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.

1.4 *Interferences.* The TRS 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<sub>2</sub> and may be present in a lime kiln exit stack, would be a positive interferent.

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<sub>2</sub>S to be absorbed before oxidation. Proper use of the particulate filter, described in Section 2.1.3 of Method 16A, will eliminate this interference.

Carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) 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<sub>2</sub>. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO<sub>2</sub> in diluent gas. The CO<sub>2</sub> level should be approximately 10 percent for the case with CO<sub>2</sub> present. The two chromatograms should show agreement within the precision limits of Section 1.5.

1.5 *Precision and Accuracy.* The GC/FPD and dilution calibration precision and drift, and the system calibration accuracy are the same as in Method 16, Sections 4.1 to 4.3.

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.

### 2. *Apparatus*

2.1 *Sampling.* A sampling train is shown in Figure 16B-1. Modifications to the apparatus are accepted provided the system performance check is met.

Figure 16B-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

2.1.1 *Probe, Probe Brush, Particulate Filter, SO<sub>2</sub> Scrubber, Combustion Tube, and Furnace.* Same as in

Method 16A, Sections 2.1.1 to 2.1.6.

2.1.2 *Sampling Pump*. Leakless Teflon-coated diaphragm type or equivalent.

2.2 *Analysis*.

2.2.1 *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 5.2, 5.4, and 5.5.

2.2.2 *Gas Chromatograph Columns*. Same as in Method 16, Section 12.1.4.1.1. Other columns with demonstrated ability to resolve SO<sub>2</sub> and be free from known interferences are acceptable alternatives.

3. *Reagents*

Same as in Method 16, Section 6, except the following:

3.1 *Calibration Gas*. SO<sub>2</sub> 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<sub>2</sub> permeation tubes, National Bureau of Standards traceable cylinder gases containing SO<sub>2</sub> in nitrogen may be used for calibration. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

3.2 *Recovery Check Gas*. Hydrogen sulfide (100 ppm or less) in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in Section 7.1 of Method 16A, or gas chromatography where the instrument is calibrated with an H<sub>2</sub>S 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.

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, an H<sub>2</sub>S concentration in the range of the stack gas or within 20 percent of the standard can be generated.

3.3 *Combustion Gas*. Gas containing less than 50 ppb reduced sulfur compounds and less than 10 ppm 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.

4. *Pretest Procedures*

Same as in Method 16, Section 7.

5. *Calibration*

Same as in Method 16, Section 8, except SO<sub>2</sub> is used instead of H<sub>2</sub>S.

6. *Sampling and Analysis Procedure*

6.1 *Sampling*. Before any source sampling is done, conduct a system performance check as detailed in Section 7.1 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 through the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the precise dilution factor as in Section 8.5 of Method 16.

6.2 *Analysis*. Pass aliquots of diluted sample through the SO<sub>2</sub> scrubber and oxidation furnace, and then inject into the GC/FPD analyzer for analysis. The rest of the analysis is the same as in Method 16, Sections 9.2.1 and 9.2.2.

## 7. Post-Test Procedures

7.1 *System Performance Check*. Same as in Method 16A, Section 4.3. Sufficient numbers of sample injections should be made so that the precision requirements of Section 4.1 of Method 16 are satisfied.

7.2 *Recalibration*. Same as in Method 16, Section 10.2.

7.3 *Determination of Calibration Drift*. Same as in Method 16, Section 10.3.

## 8. Calculations

### 8.1 *Nomenclature*.

C[SO<sub>2</sub>] = Sulfur dioxide concentration, ppm.

C[TRS] = Total reduced sulfur concentration as determined by Equation 16B-1, ppm.

d = Dilution factor, dimensionless.

N = Number of samples.

8.2 *SO<sub>2</sub> Concentration*. Determine the concentration of SO<sub>2</sub> (C[SO<sub>2</sub>]) directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

### 8.3 *TRS Concentration*.

$C[TRS] = (C[SO_2]) (d)$

Eq. 16B-1

### 8.4 *Average TRS Concentration*.

Avg. C[TRS] =  $\langle n \rangle \text{SIGMA } [i = 1] C[TRS] / N$

Eq. 16B-2

## 9. Example System

Same as in Method 16, Section 12. Single column systems using the column in Section 12.1.4.1.1 of Method 16 or a 7-ft Carbosorb B HT 100 column have been found satisfactory in resolving SO<sub>2</sub> from CO<sub>2</sub>.

## 10. Bibliography

1. Same as in Method 16, Sections 13.1 to 13.6.
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## METHOD 17 -- DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES (IN-STACK FILTRATION METHOD)

### *Introduction*

Particulate matter is not an absolute quantity; rather, it is a function of temperature and pressure. Therefore, to prevent variability in particulate matter emission regulations and/or associated test methods, the temperature and pressure at which particulate matter 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 particulate matter in an effluent gas stream; in most stationary source categories, the effect of pressure appears to be negligible.

In Method 5, 250 deg. F is established as a nominal reference temperature. Thus, where Method 5 is specified in an applicable subpart of the standards, particulate matter is defined with respect to temperature. In order to maintain a collection temperature of 250 deg. 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 particulate matter 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 heating systems, and sample at stack temperature.

This method describes an in-stack sampling system and sampling procedures for use in such cases. 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.

### *1. Principle and Applicability*

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

1.2 Applicability. This method applies to the determination of particulate emissions from stationary sources for determining compliance with new source performance standards, only when specifically provided for in an applicable subpart of the standards. 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 4.1.2).

### *2. Apparatus*

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 17-1. Construction details for many, but not all, of the train components are given in APTD-0581 (Citation 2 in

Bibliography); for changes from the APTD-0581 document and for allowable modifications to Figure 17-1, consult with the Administrator.

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

[SEE FIGURE IN ORIGINAL]

The operating and maintenance procedures for many of the sampling train components are described in APTD-0576 (Citation 3 in Bibliography). Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass, with sharp, tapered leading edge. The angle of taper shall be 30 deg. and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing. Other materials of construction may be used subject to the approval of the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) -- or larger if higher volume sampling trains are used -- inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1.

2.1.2 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.

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

2.1.4 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator; the pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity (see Figure 17-1). The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane during sampling (see Method 2, Figure 2-6b). It is recommended: (1) that the pitot tube have a known baseline coefficient, determined as outlined in Section 4 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 (0.75 in.) free-space between the nozzle and pitot tube shown in Figure 17-1, is based on a 1.3 cm (0.5 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 (0.75 in.) with the largest sized nozzle in place.

Source-sampling assemblies that do not meet the minimum spacing requirements of Figure 17-1 (or the equivalent of these requirements, e.g., Figure 2-7 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.

2.1.5 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (DELTA p) readings, and the other, for orifice differential pressure readings.

2.1.6 Condenser. It is recommended that the impinger system described in Method 5 be used to determine the moisture content of the stack gas. Alternatively, any system that allows measurement of both the water



condensed and the moisture leaving the condenser, each to within 1 ml or 1 g, may be used. The moisture leaving the condenser can be measured either by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a silica gel trap with exit gases kept below 20 deg. C (68 deg. F) and determining the weight gain.

Flexible tubing may be used between the probe extension and condenser. If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.7 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3 deg. C (5.4 deg. F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 17-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.8 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.9 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3.

The temperature sensor shall be attached to either the pitot tube or to the probe extension, in a fixed configuration. If the temperature sensor is attached in the field, the sensor shall be placed in an interference-free arrangement with respect to the Type S pitot tube openings (as shown in Figure 17-1 or in Figure 2-7 of Method 2). Alternatively, the temperature sensor need not be attached to either the probe extension or pitot tube during sampling, provided that a difference of not more than 1 percent in the average velocity measurement is introduced. This alternative is subject to the approval of the Administrator.

## 2.2 Sample Recovery.

2.2.1 Probe Nozzle Brush. Nylon bristle brush with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

2.2.2 Wash Bottles -- Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.3 Analysis.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 mg.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

### 3. *Reagents*

#### 3.1 Sampling.

3.1.1 Filters. The in-stack filters shall be glass mats or thimble fiber filters, without organic binders, and shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency tests shall be conducted in accordance with ASTM Standard Method D2986-71 (Reapproved 1978) (incorporated by reference -- see § 60.17). Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175 deg. C (350 deg. F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Crushed Ice.

3.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.1.5 Water. Same as in Method 5, section 3.1.3.

3.2 Sample Recovery. Acetone, reagent grade, 0.001 percent residue, in glass bottles. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers. Thus, acetone blanks shall be run prior to field use and only acetone with

low blank values (0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

### 3.3 Analysis.

#### 3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

## 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. All components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers 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 need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper size on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20 +/- 5.6 deg. C (68 +/- 10 deg. F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105 deg. C (220 deg. F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. 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: (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 Citation 10 in Bibliography). Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

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.

[SEE FIGURE IN ORIGINAL]

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

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.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval if specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

If impingers are used to condense stack gas moisture, prepare them as follows: place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the 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.

If some means other than impingers is used to condense moisture, prepare the condenser (and, if appropriate, silica gel for condenser outlet) for use.

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.

4.1.4 Leak Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, 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. Turn on the pump and draw a vacuum of at least 380 mm Hg (15 in. Hg); note that a lower vacuum may be used, provided that it is not exceeded during the test. Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m<sup>3</sup>/min. (0.02 cfm), whichever is less, is unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse direction of by-pass valve. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m<sup>3</sup>/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-Test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m<sup>3</sup>/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain a sampling rate such that sampling is within 10 percent of true isokinetic, unless otherwise specified by the Administrator.

For each run, record the data required on the example data sheet shown in Figure 17-3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 17-3 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

FIGURE 17-3 -- PARTICULATE FIELD DATA

[SEE FIGURE IN ORIGINAL]

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin

sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment to the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is  $0.85 \pm 0.02$ , and the stack gas equivalent density (dry molecular weight) is equal to  $29 \pm 4$ . APTD-0576 details the procedure for using the nomographs. If  $C[p]$  and  $M[d]$  are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Citation 7 in Bibliography) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes, to minimize chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain a temperature of less than 20 deg. C (68 deg. F) at the condenser outlet; this will prevent excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter holder assembly be used rather than attempting to change the filter itself. Before a new filter holder is installed, conduct a leak check, as outlined in Section 4.1.4.2. The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator. Note that when two or more trains are used, a separate analysis of the collected particulate from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the particulate catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Section 3.1 of Method 2; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Section 6.11) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample Recovery. 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.

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.

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.

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.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly 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 note any abnormal conditions. Treat the samples as follows:

*Container No. 1.* Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves 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 petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

*Container No. 2.* Taking care to see that dust on the outside of the probe nozzle or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, fitting, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. 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 Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the fitting in a similar way until no visible particles remain. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Rinse the brush with acetone and quantitatively collect these washings in the sample container. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease (if applicable), clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make final rinse of the brush and filter holder. After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

*Container No. 3.* If silica gel is used in the condenser system for moisture content determination, note the color

of the gel to determine if it has been completely spent; make a notation of its condition. Transfer the silica gel back to its original container and seal. A funnel may make it easier to pour the silica gel without spilling, and a rubber policeman may be used as an aid in removing the silica gel. It is not necessary to remove the small amount of dust particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 under "Analysis."

*Condenser Water.* Treat the condenser or impinger water as follows: make a notation of any color or film in the liquid catch. Measure the liquid volume to within +/- 1 ml by using a graduated cylinder or, if a balance is available, determine the liquid weight to within +/- 0.5 g. Record the total 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.

4.3 Analysis. Record the data required on the example sheet shown in Figure 17-4. Handle each sample container as follows:

*Container No. 1.* Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at the average stack temperature or 105 deg. C (220 deg. F), whichever is less, for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at the average stack temperature or 105 deg. C (220 deg. F), whichever is less, for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

FIGURE 17-4 -- ANALYTICAL DATA

Plant

Date

Run No.

Filter No.

Amount liquid lost during transport

Acetone blank volume, ml

Acetone wash volume, ml

Acetone blank concentration, mg/mg (Equation 17-4)

Acetone wash blank, mg (Equation 17-5)

Container number	Weight of particulate collected, mg		Weight gain
	Final weight	Tare weight	



1  
2  
Total  
Less acetone  
blank  
Weight of particulate  
matter

Volume of  
liquid  
water  
collected  
Impinger Silica gel  
volume,ml weight, g

Final  
Initial  
Liquid collected  
Total volume  
collected                   g\*    ml

\* Convert weight of water to volume by dividing total weight increase by density of water (1g/ml).

Increase, g / (1 g/ml) = Volume water, ml

*Container No. 2.* 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 to +/- 1 ml or gravimetrically to +/- 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

*Container No. 3.* This step may be conducted in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

*"Acetone Blank" Container.* Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

## 5. Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. If the pitot tube is placed in an interference-free arrangement with respect to the other probe assembly components, its baseline (isolated tube) coefficient shall be determined as outlined in Section 4 of Method 2. If the probe assembly is not interference-free, the pitot tube assembly coefficient shall be determined by calibration, using methods subject to the approval of the Administrator.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values.

Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m<sup>3</sup> / min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m<sup>3</sup> / min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

NOTE: If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.5 Leak Check of Metering System Shown in Figure 17-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 17-5). Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

Figure 17-5. Leak Check of meter box.

[See Figure in Original]

5.6 Barometer. Calibrate against a mercury barometer.

## 6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

### 6.1 Nomenclature.

A[n] = Cross-sectional area of nozzle,  $m^2$  ( $ft^2$ ).

B[ws] = Water vapor in the gas stream, proportion by volume.

C[a] = Acetone blank residue concentration, mg/mg.

c[s] = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L[a] = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to  $0.00057 m^3/min$  (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L[i] = Individual leakage rate observed during the leak check conducted prior to the "i<sup>th</sup>" component change (i = 1, 2, 3 . . . n),  $m^3/min$  (cfm).

L[p] = Leakage rate observed during the post-test leak check,  $m^3/min$  (cfm).

m[a] = Mass of residue of acetone after evaporation, mg.

m[n] = Total amount of particulate matter collected, mg.

M[W] = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P[bar] = Barometric pressure at the sampling site, mm Hg (in. Hg).

P[s] = Absolute stack gas pressure, mm Hg (in. Hg).

P[std] = Standard absolute pressure, 760 mm Hg (29.92 in Hg).

R = Ideal gas constant,  $0.062326 mm\ Hg \cdot m^3 / (degrees\ K \cdot g \cdot mole)$  ( $21.85 in.\ Hg \cdot ft^3 / (degrees\ R \cdot lb \cdot mole)$ ).

T[m] = Absolute average dry gas meter temperature (see Figure 17-3), deg. K ( deg. R).

T[s] = Absolute average stack gas temperature (see Figure 17-3), degrees K (degrees R).

T[std] = Standard absolute temperature, 293 deg. K (528 deg. R).

V[a] = Volume of acetone blank, ml.

V[aw] = Volume of acetone used in wash, ml.

V[lc] = Total volume of liquid collected in impingers and silica gel (see Figure 17-4),ml.

V[m] = Volume of gas sample as measured by dry gas meter, dcm (dcf).

V[m(std)] = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V[w(std)] = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V[s] = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 17, m/sec (ft/sec).

W[a] = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration coefficient.

DELTA H = Average pressure differential across the orifice meter (see Figure 17-3), mm H<sub>2</sub>O (in. H<sub>2</sub>O).

rho[a] = Density of acetone, mg/ml (see label on bottle).

rho[W] = Density of water, 0.9982 g/ml (0.002201 lb/ml).

theta = Total sampling time, min.

theta[1] = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

theta[p] = Sampling time interval, from the final (n<th>) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

6.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 17-3).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 deg. C, 760 mm Hg or 68 deg. F, 29.92 in. Hg) by using Equation 17-1.

$$V[m(std)] = V[m]Y \times (T[std] / T[m]) \times P[bar] + DELTA H / [13.6] / P[std] = K[1]V[m]Y \times P[bar] + (DELTA H / 13.6) / T[m]$$

Eq. 71-1

Where:

$K[1] = 0.3858 \text{ deg. K/mm Hg}$  for metric units;  $17.64 \text{ deg. R/in. Hg}$  for English units.

NOTE: Equation 17-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds  $L[a]$ . If  $L[p]$  or  $L[i]$  exceeds  $L[a]$ , Equation 17-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace  $V[m]$  in Equation 17-1 with the expression:

$$[V[m] - (L[p] - L[a]) \text{ THETA}]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace  $V[m]$  in Equation 17-1 by the expression:

$$[V[m] - (L[1] - L[a]) \times \text{theta}[1] - \text{SIGMA } [i = 2] \times (L[i] - L[a]) \times \text{theta}[i] - (L[p] - L[a]) \times \text{theta}[p]]$$

and substitute only for those leakage rates ( $L[i]$  or  $L[p]$ ) which exceed  $L[a]$ .

6.4 volume of Water Vapor.

$$V[w(\text{std})] = V[lc] \times (p[w] / M[w]) \times (RT[\text{std}] / P [\text{std}]) = K[2] V[lc]$$

Eq. 17-2

Where:

$K[2] = 0.001333 \text{ m}^3/\text{ml}$  for metric units;  $0.04707 \text{ ft}^3/\text{ml}$  for English units.

6.5 Moisture Content.

$$B[ws] = V[w(\text{std})] / V[m(\text{std}) + V[w(\text{std})]]$$

Eq. 17-3

6.6 Acetone Blank Concentration.

$$C[a] = m[a] / V[a] \rho[a]$$

Eq. 17-4

6.7 Acetone Wash Blank.

$$W[a] = C[a]V[aw] \rho[a]$$

Eq. 17-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 17-4).

NOTE: Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

## 6.9 Particulate Concentration

$$c[s] = (0.001 \text{ g/mg}) (m[n] / V[m(\text{std})])$$

Eq. 17-6

## 6.10 Conversion Factors:

From	To	Multiply by
scf	m <sup>3</sup>	0.02832
g/ft <sup>3</sup>	gr/ft <sup>3</sup>	15.43
g/ft <sup>3</sup>	lb/ft <sup>3</sup>	2.205X10 <sup>-3</sup>
g/ft <sup>3</sup>	g/m <sup>3</sup>	35.31

## 6.11 Isokinetic Variation.

### 6.11.1 Calculation from Raw Data.

$$I = 100 T[S] (K[3] V[lc] + (V[m] Y / t[m]) X (P[\text{bar}] + \text{DELTAH} / 13.6)) / 60 \theta V[s] P[s] A[n]$$

Eq. 17-7

Where:

K[3] = 0.003454 mm Hg-m<sup>3</sup>/ml-deg. K for metric units; 0.002669 in. Hg-ft<sup>3</sup>/ml-deg. R for English units.

### 6.11.2 Calculation from Intermediate Values.

$$I = T[s] V[m(\text{std})] P[\text{std}] 100 / T[\text{std}] v[s] \theta A[n] P[s] (I-B[\text{ws}])$$
$$= K[4] T[s] V[m(\text{std})] / P[s] v[s] A[n] \theta (I-B[\text{ws}])$$

Eq. 17-8

Where:

K[4] = 4.320 for metric units; 0.09450 for English units.

6.12 Acceptable Results. If 90 percent <I < 110 percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or, if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 in Bibliography to make judgments. Otherwise, reject the results and repeat the test.

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## METHOD 18 -- MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

### *Introduction*

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

### *1. Applicability and Principle*

1.1 Applicability. This method applies to the analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources.

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

### *1.2 Principle.*

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 before-hand. 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 detection saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

## *2. Range and Sensitivity*

2.1 Range. The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

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

## *3. Precision and Accuracy*

Gas chromatographic techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Duplicate analyses are within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

## *4. Interferences*

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

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

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

To Assure consistent detector response, calibration gases are contained in dry air. To 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.

## *5. Presurvey and Presurvey Sampling.*

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.

5.1 Apparatus. This apparatus list also applies to Sections 6 and 7.

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



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

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

5.1.4 Flowmeters. To measure flow rates.

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

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

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

5.1.8 Tubing Fittings. To plumb GC and gas cylinders.

5.1.9 Septums. For syringe injections.

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

5.1.11 Soap Film Flow Meter. To determine flow rates.

5.1.12 Tedlar Bags. 10- and 50-liter capacity, for preparation of standards.

5.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to +/- 2 percent, for preparation of gas standards.

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

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

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

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

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

5.1.19 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.

5.1.20 Barometer. To measure barometric pressure.

5.2 Reagents.

5.2.1 Deionized Distilled Water.

5.2.2 Methylene Dichloride.

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

5.2.4 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.

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

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

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

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

### 5.3 Sampling.

5.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples can be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene dichloride. Clean all glass 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 deg. C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Grease the stopcocks with stopcock grease and return them to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape.

Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

5.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

5.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in Section 5.3.1.1. Place the filter end of the probe at the centroid of the duct, 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 the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

5.3.2 Flexible Bag Procedure. Tedlar or aluminized Mylar bags can also be used to obtain the presurvey sample. Use new bags, and leak check them before field use. In addition, check the bag before use for contamination by

filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak check and sample collection procedures given in Section 7.1.

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

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

5.5 Collection of Presurvey Samples with Adsorption Tube. Follow Section 7.4 for presurvey sampling.

## 6. *Analysis Development*

### 6.1 Selection of GC Parameters.

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

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

Plants with analytical laboratories may also be able to provide information on appropriate analytical procedures.

6.1.2 Preliminary GC Adjustment. Using the standards and column obtained in Section 6.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

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

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

Use the GC conditions determined by the procedures of Section 6.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier

flow rate, chart speed, and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid samples, dilution with solvent is appropriate. Use the standard curves (Section 6.3) to obtain an estimate of the concentrations.

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

6.2 Calibration Standards. 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 available, commercial cylinder gases may be used if their concentrations have been certified by direct analysis.

If samples are collected in adsorbent tubes (charcoal, XAD-2, Tenax, etc.), prepare or obtain standards in the same solvent used for the sample extraction procedure. Refer to Section 7.4.3.

Verify the stability of all standards for the time periods they are used. If gas standards are prepared in the laboratory, use one or more of the following procedures.

6.2.1 Preparation of Standards from High Concentration Cylinder Standards. Obtain enough high concentration cylinder standards to represent all the organic compounds expected in the source samples.

Use these high concentration standards to prepare lower concentration standards by dilution, as shown by Figures 18-5 and 18-6.

To prepare the diluted calibration samples, calibrated rotameters are normally used to meter both the high concentration calibration gas and the diluent gas. Other types of flowmeters and commercially available dilution systems can also be used.

Calibrate each flowmeter before use by placing it between the diluent gas supply and suitably sized bubble meter, spirometer, or wet test meter. Record all data shown on Figure 18-4. While it is desirable to calibrate the cylinder gas flowmeter with cylinder gas, the available quantity and cost may preclude it. The error introduced by using the diluent gas for calibration is insignificant for gas mixtures of up to 1,000 to 2,000 ppm of each organic component.

Once the flowmeters are calibrated, connect the flowmeters to the calibration and diluent gas supplies using 6-mm Teflon tubing. Connect the outlet side of the flowmeters through a connector to a leak-free Tedlar bag as shown in Figure 18-5. (See Section 7.1 for bag leak-check procedures.) Adjust the gas flow to provide the desired dilution, and fill the bag with sufficient gas for GC calibration. Be careful not to overfill and cause the bag to apply additional pressure on the dilution system. Record the flow rates of both flowmeters, and the laboratory temperature and atmospheric pressure. Calculate the concentration C[s] in ppm of each organic in the diluted gas as follows:

$$C[s] = 10^6 (X q[c]) / q[c] + q[d]$$

EQ. 18-1

where:

$10^{(6)}$  = Conversion to ppm.

X = Mole or volume fraction of the organic in the calibration gas to be diluted.

q[c] = Flow rate of the calibration gas to be diluted.

q[d] = Diluent gas flow rate.

Single-stage dilutions should be used to prepare calibration mixtures up to about 1:20 dilution factor.

For greater dilutions, a double dilution system is recommended, as shown in Figure 18-6. Fill the Tedlar bag with the dilute gas from the second stage. Record the laboratory temperature, barometric pressure, and static pressure readings. Correct the flow reading for temperature and pressure. Calculate the concentration C[s] in ppm of the organic in the final gas mixture as follows:

$$C[s] = 10^{(6)} X (q[c1] / (q[c1] + q[d1])) X (q[c2] / (q[c2] + q[d2]))$$

Eq. 18-2

Where:

$10^{(6)}$  = Conversion to ppm.

X = Mole or volume fraction of the organic in 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[d1] = Flow rate of diluent gas in stage 1.

q[d2] = Flow rate of diluent gas in stage 2.

Further details of the calibration methods for flowmeters and the dilution system can be found in Citation 21 in the Bibliography.

6.2.2 Preparation of Standards from Volatile Materials. Record all data shown on Figure 18-3.

6.2.2.1 Gas Injection Technique. This procedure is applicable to organic compounds that exist entirely as a gas at ambient conditions. Evacuate a 10-liter Tedlar bag that has passed a leak-check (see Section 7.1), and meter in 5.0 liters of air or nitrogen through a dry gas meter that has been calibrated in a manner consistent with the procedure described in Section 5.1.1 of Method 5. While the bag is filling use a 0.5-ml syringe to inject a known quantity of "pure" gas of the organic compound through the wall of the bag, or through a septum-capped tee at the bag inlet. Withdraw the syringe needle, and immediately cover the resulting hole with a piece of masking tape. In a like manner, prepare dilutions having other concentrations. Prepare a minimum of three concentrations. Place each bag on a smooth surface, and alternately depress opposite sides of the bag 50 times to mix the gases. Record the average meter temperature and pressure, the gas volume and the barometric pressure. Record the syringe temperature and pressure before injection.

Calculate each organic standard concentration C, in ppm as follows:

$$C[s] = G[v] \times 10^6 \times 293 / T[s] \times P[s] / 760 / V[m] \times Y \times 293 / T[m] \times P[m] / 760 \times 1000$$
$$= G[v] \times 10^3 \times P[s] / T[s] \times T[m] / P[m] / Y[m] \times Y$$

where:

G[v] = Gas volume or organic compound injected, ml.

10<sup>6</sup> = Conversion to ppm.

P[s] = Absolute pressure of syringe before injection, mm Hg.

T[s] = Absolute temperature of syringe before injection, deg. K.

V[m] = Gas volume indicated by dry gas meter, liters.

Y = Dry gas meter calibration factor, dimensionless.

P[m] = Absolute pressure of dry gas meter, mm Hg.

T[m] = Absolute temperature of dry gas meter, deg. K.

1000 = Conversion factor, ml/liter.

6.2.2.2 Liquid Injection Technique. Use the equipment shown in Figure 18-8. Calibrate the dry gas meter as described in Section 6.2.2.1 with a wet test meter or a spirometer. Use a water manometer for the pressure gauge and glass, Teflon, brass, or stainless steel for all connections. Connect a valve to the inlet of the 50-liter Tedlar bag.

To prepare the standards, assemble the equipment as shown in Figure 18-8, and leak-check the system. Completely evacuate the bag. Fill the bag with hydrocarbon-free air, and evacuate the bag again. Close the inlet valve.

Turn on the hot plate, and allow the water to reach boiling. Connect the bag to the impinger outlet. Record the initial meter reading, open the bag inlet valve, and open the cylinder. Adjust the rate so that the bag will be completely filled in approximately 15 minutes. Record meter pressure and temperature, and local barometric pressure.

Allow the liquid organic to equilibrate to room temperature. Fill the 1.0- or 10-microliter syringe to the desired liquid volume with the organic. Place the syringe needle into the impinger inlet using the septum provided, and inject the liquid into the flowing air stream. Use a needle of sufficient length to permit injection of the liquid below the air inlet branch of the tee. Remove the syringe.

When the bag is filled, stop the pump, and close the bag inlet valve. Record the final meter reading, temperature, and pressure.

Disconnect the bag from the impinger outlet, and either set it aside for at least 1 hour, or massage the bag to insure complete mixing.

Measure the solvent liquid density at room temperature by accurately weighing a known volume of the material

on an analytical balance to the nearest 1.0 milligram. A ground-glass stoppered 25-mil volumetric flask or a glass-stoppered specific gravity bottle is suitable for weighing. Calculate the result in terms of g/ml. As an alternative, literature values of the density of the liquid at 20 deg. C may be used.

Calculate each organic standard concentration C[s] in ppm as follows:

$$C[s] = \frac{L[v] \times \rho \times (24.055 \times 10^6)}{V[m] \times Y \times 293 / T[m] \times P[m] / 760 \times 1000} = 6.24 \times 10^4 \times \frac{L[v] \times \rho \times T[m] / M \times V[m] \times Y \times P[m]}$$

Eq. 18-4

where:

L[v] = Liquid volume of organic injected, ml.

$\rho$  = Liquid organic density as determined, g/ml.

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

24.055 = Ideal gas molar volume at 293 deg. K and 760 mm Hg, liters/g-mole.

$10^6$  = Conversion to ppm.

1000 = Conversion factor, ml/l.

6.3 Preparation of Calibration Curves. Establish proper GC conditions, then flush the sampling loop for 30 seconds at a rate of 100 ml/min. 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. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their average. The average value multiplied by the attenuator factor is then the calibration area value for the concentration.

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 squares line.

6.4 Relative Response Factors. The calibration curve generated from the standards for a single organic can usually be related to each of the individual GC response curves that are developed in the laboratory for all the compounds in the source. In the field, standards for that single organic can then be used to "calibrate" the GC for all the organics present. This procedure should first be confirmed in the laboratory by preparing and analyzing calibration standards containing multiple organic compounds.

6.5 Quality Assurance for Laboratory Procedures. Immediately after the preparation of the calibration curves and prior to the presurvey sample analysis, the analysis audit described in 40 CFR Part 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis," should be performed. The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 18-3 and 18-7. The audit analyses should agree with the audit concentrations within 10 percent. When available, the tester may obtain audit cylinders by contacting: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina, 27711. Audit cylinders obtained from a commercial gas manufacturer may be used provided that (a) the gas manufacturer certifies the audit cylinder in a manner similar to the procedure described in 40 CFR Part 61, Appendix B, Method 106, Section 5.2.3.1, and (b) the gas manufacturer obtains an independent analysis of the audit cylinders to verify this analysis. Independent analysis is defined as an analysis performed by an individual

other than the individual who performs the gas manufacturer's analysis, while using calibration standards and analysis equipment different from those used for the gas manufacturer's analysis. Verification is complete and acceptable when the independent analysis concentration is within 5 percent of the gas manufacturer's concentration.

## *7. Final Sampling and Analysis Procedure*

Considering safety (flame hazards) and the source conditions, select an appropriate sampling and analysis procedure (Section 7.1, 7.2, 7.3, or 7.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique. If the source temperature is below 100 deg. C, and the organic concentrations are suitable for the detector to be used, use the direct interface method. If the source gases require dilution, use a dilution interface and either the bag sample or adsorption tubes. The choice between these two techniques will depend on the physical layout of the site, the source temperature, and the storage stability of the compounds if collected in the bag. Sample polar compounds by direct interfacing or dilution interfacing to prevent sample loss by adsorption on the bag.

### 7.1 Integrated Bag Sampling and Analysis.

**7.1.1 Evacuated Container Sampling Procedure.** In this procedure, the bags are filled by evacuating the rigid airtight containers that hold the bags. Use a field sample data sheet as shown in Figure 18-10. Collect triplicate sample from each sample location.

#### 7.1.1.1 Apparatus.

**7.1.1.1.1 Probe.** Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with 6.4-mm OD Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

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

**7.1.1.1.3 Needle Valve.** To control gas flow.

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

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

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

**7.1.1.2 Sampling Procedure.** To obtain a sample, assemble the sample train as shown in Figure 18-9. Leak check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack, or at a point no closer to the walls than 1 m, and start the pump with the needle valve adjusted to yield a flow of 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 18-10. Protect the Tedlar bag and its container from sunlight. When possible, perform the analysis within 2 hours of sample collection.



7.1.2 Direct Pump Sampling Procedure. Follow 7.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of stainless steel or some other material not affected by the stack gas. Leak check the system, and then purge with stack gas before the connecting to the previously evacuated bag.

7.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 7.1.1 except replace the pump with another evacuated can (see Figure 18-9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

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

In the first procedure, heat the box containing the sample bag to the source temperature, provided the components of the bag and the surrounding box can withstand this temperature. Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to source temperature until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

To use the second procedure, prefill the Tedlar bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 6.2.2.2), but eliminate the midjet impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors periodically through dilution and analysis of gases of known concentration.

#### 7.1.5 Analysis of Bag Samples.

7.1.5.1 Apparatus. Same as Section 5. A minimum of three gas standards are required.

7.1.5.2 Procedure. Establish proper GC operating conditions as described in Section 6.3, 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 gas from one of the three calibration mixtures, and activate the valve. Obtain at least two chromatograms for the mixture. The results are acceptable when the peak areas from two consecutive injections agree to within 5 percent of their average. If they do not, run additional analyses 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 the same manner. Prepare a calibration curve as described in Section 6.3.

Analyze the source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified for that bag. Follow the specifications on replicate analyses specified for the calibration gases. Record the data listed in Figure 18-11. If certain items do not apply, use the notation "N.A." After all samples have been analyzed, repeat the analyses of the calibration gas mixtures, and generate a second calibration curve. Use an average of the two curves to determine the sample gas concentrations. If the two calibration curves differ by more than 5 percent from their mean value, then report the final results by comparison to both calibration curves.

7.1.6 Determination of Bag Water Vapor Content. Measure and record the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content 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 7.1.4, determine the stack gas water content by Method 4.

7.1.7 Quality Assurance. Immediately prior to the analysis of the stack gas samples, perform audit analyses as described in Section 6.5. The audit analyses must agree with the audit concentrations within 10 percent. If the results are acceptable, proceed with the analyses of the source samples. If they do not agree within 10 percent, then determine the reason for the discrepancy, and take corrective action before proceeding.

7.1.8 Emission Calculations. From the average calibration curve described in Section 7.1.5., 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 as follows:

$$C[c] = C[s] P[r] T[i] F[r] / P[i] T[r] (1-B[ws])$$

Eq. 18-5

where:

C[s] = Concentration of the organic from the calibration curve, ppm.

P[r] = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.

T[i] = Sample loop temperature at the time of sample analysis, deg. K.

F[r] = Relative response factor (if applicable, see Section 6.4).

P[i] = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.

T[r] = Reference temperature, the temperature of the sample loop recorded during calibration, deg. K.

B[ws] = Water vapor content of the bag sample or stack gas, proportion by volume.

7.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. Adhere to all safety requirements with this method.

7.2.1 Apparatus.

7.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as required by duct temperature, 6.4-mm OD, enlarged at duct end to contain glass wool plug. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining duct temperature.

7.2.1.2 Sample Lines. 6.4-mm OD Teflon lines, heat-traced to prevent condensation of material.

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

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

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

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

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

7.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

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

7.2.1.10 Gas Cylinders. Carrier gas (helium or nitrogen), and oxygen and hydrogen for a flame ionization detector (FID) if one is used.

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

7.2.1.12 Recorder/Integrator. To record results.

7.2.2 Procedure. To obtain a sample, assemble the sampling system as shown in Figure 18-12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the source temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature of 0 to 3 deg. C above the source temperature. While the probe and heated line are being heated, disconnect the sample line from the gas sampling valve, and attach the line from the calibration gas mixture. Flush the sample loop with calibration gas and analyze a portion of that gas. Record the results. After the calibration gas sample has been flushed into the GC instrument, turn the gas sampling valve to flush position, then reconnect the probe sample line to the valve. 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 sample using the same conditions as for the calibration gas mixture. Repeat the analysis on an additional sample. Measure the peak areas for the two samples, and if they do not agree to within 5 percent of their mean value, analyze additional samples until two consecutive analyses meet this criteria. Record the data. After consistent results are obtained, remove the probe from the source and analyze a second calibration gas mixture. Record this calibration data and the other required data on the data sheet shown in Figure 18-11, deleting the dilution gas information.

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

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

7.2.4 Quality Assurance. Same as Section 7.1.7. Introduce the audit gases in the sample line immediately following the probe.

7.2.5 Emission Calculations. Same as Section 7.1.8.

7.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the Section 7.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged

so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

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

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

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

7.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to 6.4-mm OD Teflon tubing.

7.3.1.4 Flowmeters. Two, for measurement of diluent gas, expected delivery flow rate to be 1,350 cc/min.

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

7.3.1.6 Heated Box. Suitable for being heated to 120 degrees C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) The heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18-13.

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

The heated box shown in Figure 18-13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

7.3.2 Procedure. Assemble the apparatus by connecting the heated box, shown in Figure 18-13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple to 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 deg. C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds. Verify the operation of the dilution system by analyzing a high concentration gas of known composition through either the 10:1 or 100:1 dilution stages, as appropriate. (If necessary, vary the flow of the diluent gas to obtain other dilution ratios.) Determine the concentration of the diluted calibration gas using the dilution factor and the calibration curves prepared in the laboratory. Record the pertinent data on the data sheet shown in Figure 18-11. If the data on the diluted calibration gas are not within 10 percent of the expected values, determine whether the chromatograph or the dilution system is in error, and correct it. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop, bypassing the dilution system. If these analyses are not within acceptable limits, correct the dilution system to provide the desired dilution factors. Make this correction by diluting a high-concentration standard gas mixture to adjust the dilution ratio as required.

Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards. Repeat the analyses until two consecutive valves do not vary by more than 5 percent from their mean value are obtained.

Repeat the analysis of the calibration gas mixtures to verify equipment operation. Analyze the two field audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

7.3.3 Determination of Stack Gas Moisture Content. Same as Section 7.2.3.

7.3.4 Quality Assurance. Same as Section 7.2.4.

7.3.5 Emission Calculations. Same as Section 7.2.5, with the dilution factor applied.

7.4 Adsorption Tube Procedure (Alternative Procedure). It is suggested that the tester refer to the National Institute of Occupational Safety and Health (NIOSH) method for the particular organics to be sampled. The principal interferent will be water vapor. If water vapor is present at concentrations above 3 percent, silica gel should be used in front of the charcoal. Where more than one compound is present in the emissions, then develop relative adsorptive capacity information.

7.4.1 Additional Apparatus. In addition to the equipment listed in the NIOSH method for the particular organic(s) to be sampled, the following items (or equivalent) are suggested.

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

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

7.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices to provide pumping rates from approximately 10 to 100 cc/min.

7.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within +/- 1 percent, to calibrate pump.

7.4.1.5 Stopwatch. To time sampling and pump rate calibration.

7.4.1.6 Adsorption Tubes. Similar to ones specified by NIOSH, except the amounts of adsorbent per primary/backup sections are 800/200 mg for charcoal tubes and 1040/260 mg for silica gel tubes. As an alternative, the tubes may contain a porous polymer adsorbent such as Tenax GC or XAD-2.

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

7.4.1.8 Rotameter. 0 to 100 cc/min, to detect changes in flow rate during sampling.

7.4.2 Sampling and Analysis. It is suggested that the tester follow the sampling and analysis portion of the respective NIOSH method section entitled "Procedure." Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

Use a sample probe, if required, 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 absorption tubes. Several absorption tubes can be connected in series, if the extra absorptive capacity is needed. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight absorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. When more than one organic is present in the emissions, then develop relative absorptive capacity information. If water vapor is present in the sample at concentrations above 2 to 3 percent, the absorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Analyze the audit samples (see Section 7.4.4.3), then the emission samples. Repeat the analysis of each sample until the relative deviation of two consecutive injections does not exceed 5 percent.

7.4.3 Standards and Calibration. The standards can be prepared according to the respective NIOSH method. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses. Prepare the calibration curve by using the least squares method.

#### 7.4.4 Quality Assurance.

7.4.4.1 Determination of Desorption Efficiency. During the testing program, determine the desorption efficiency in the expected sample concentration range for each batch of adsorption media to be used. Use an internal standard. A minimum desorption efficiency of 50 percent shall be obtained. Repeat the desorption determination until the relative deviation of two consecutive determinations does not exceed 5 percent. Use the average desorption efficiency of these two consecutive determinations for the correction specified in Section 7.4.4.5. If the desorption efficiency of the compound(s) of interest is questionable under actual sampling conditions, use of the Method of Standard Additions may be helpful to determine this value.

7.4.4.2 Determination of Sample Collection Efficiency. For the source samples, analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and backup), repeat the sampling with a larger sampling portion.

7.4.4.3 Analysis Audit. Immediately before the sample analyses, analyze the two audits in accordance with Section 7.4.2. The analysis audit shall agree with the audit concentration within 10 percent.

7.4.4.4 Pump Leak Checks and Volume Flow Rate Checks. Perform both of these checks immediately after sampling with all sampling train components in place. Perform all leak checks according to the manufacturer's instructions, and record the results. Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

7.4.4.5 Calculations. All calculations can be performed according to the respective NIOSH method. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results by dividing by the desorption efficiency (decimal value). Report results as ppm by volume, dry basis.

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

SOURCE: [36 FR 24877, Dec. 23, 1971]

AUTHORITY: 42 U.S.C. 7401, 7411, 7414, 7416, and 7601.

Title 40 -- Protection of Environment; Revised as of July 1, 1991

CHAPTER I -- ENVIRONMENTAL PROTECTION AGENCY  
SUBCHAPTER C -- AIR PROGRAMS

PART 60 -- STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

§ 60. Appendix A to Part 60 -- Test Methods [PART VI OF VII]

**40 CFR 60. Appendix A** to Part 60

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Figure 18-1. Preliminary survey data sheet.

[SEE FIGURE IN ORIGINAL]

Figure 18-1 (continued). Preliminary survey data sheet.

[SEE FIGURE IN ORIGINAL]



Figure 18-2. Chromatographic conditions data sheet.

[SEE FIGURE IN ORIGINAL]

### Preparation of Standards in Tedlar Bags and Calibration Curve

Standards Preparation Data:	Standard s		
	Mixture # 1	Mixture # 2	Mixture # 3

Organic:

Bag number or identification

Dry gas meter calibration factor

Final meter reading (liters)

Initial meter reading (liters)

Metered volume (liters)

Average meter temperature (deg. K)

Average meter pressure, gauge (mm Hg)

Average atmospheric pressure (mm Hg)

Average meter pressure, absolute (mm Hg)

Syringe temperature (deg. K)  
(Section 6.2.2.1)

Syringe pressure, absolute (mm Hg)  
(Section 6.2.2.1)

Volume of gas in syringe (ml)  
(Section 6.2.2.1)

Density of liquid organic (g/ml)  
(Section 6.2.2.2)

Volume of liquid in syringe (l)  
(Section 6.2.2.2)

GC Operating Conditions:

Sample loop volume (ml)

Sample loop temperature (deg. C)

Carrier gas flow rate (ml/min)

Column temperature

Initial (deg. C)

Rate change (deg. C/min)

Final (deg. C)

Organic Peak Identification and  
Calculated Concentrations:

Injection time (24-hr clock)

Distance to peak (cm)

Chart speed (cm/min)

Organic retention time (min)

Attenuation factor

Peak height (mm)

Peak area (mm<sup>2</sup>)  
 Peak area X attenuation factor (mm<sup>2</sup>)  
 Calculated concentration (ppm)  
 (Equation 18-3 or 18-4)

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

Figure 18-3. Standards prepared in Tedlar bags and calibration curve.

### Flowmeter Calibration

Flowmeter number or identification

Flowmeter type

Calibration device (X): Bubble meter Spirometer Wet test meter

Readings at laboratory conditions:

Laboratory temperature (T[lab]) deg. K

Laboratory barometric pressure (P[lab]) mm Hg

Flow data:

	<b>Flowmeter</b>	
<b>reading</b>	<b>temp.</b>	<b>pressure</b>
(as marked)	(deg. K)	(absolute)

	<b>Calibration device</b>	
<b>Time</b>	<b>gas</b>	<b>flow</b>
(min)	volume<a>	rate<b>

a = Volume of gas measured by calibration device, corrected to standard conditions (liters).

b = Calibration device gas volume/time.

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 readings for rotameters at standard conditions Q[std] as follows:

$$Q[\text{std}] = Q[\text{lab}] \times (760 \times T[1\text{ab}] / P[1\text{ab}] \times 293)^{1/2}$$

**Flow rate**

**Flow rate**

(laboratory  
conditions)

(standard  
conditions)

Figure 18-4. Flowmeter calibration.

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

[SEE FIGURE IN ORIGINAL]

Figure 18-6. Two-stage dilution apparatus.

[SEE FIGURE IN ORIGINAL]

Preparation of Standards by Dilution of Cylinder Standard

Cylinder standard: Organic Certified concentration ppm

Standards Preparation Data:	3 Date		
Stage 1	Mixture 1	Mixture 2	Mixture 3
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Laboratory temperature (deg. 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 (ml/min)			
Calculated concentration (ppm)			
GC Operating Conditions:			

Sample loop volume (ml)  
Sample loop temperature  
(deg. C)  
Carrier gas flow rate  
(ml/min)  
Column temperature:  
    Initial (deg. C)  
    Program rate (deg.  
C/min)  
    Final (deg. C)

Organic Peak Identification  
and

Calculated Concentrations:  
Injection time (24-hr clock)  
Distance to peak (cm)  
Chart speed (cm/min)  
Retention time (min)  
Attenuation factor  
Peak area (mm<sup>2</sup>)  
Peak area X attenuation  
factor

Plot peak area X 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.

[SEE FIGURE IN ORIGINAL]

Figure 18-9. Integrated bag sampling train.

[SEE FIGURE IN ORIGINAL]

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

[SEE FIGURE IN ORIGINAL]

Figure 18-10. Field sample data sheet - Tedlar bag collection method.

[SEE FIGURE IN ORIGINAL] Plant Date Location

### 1. General Information

C) Source temperature (deg.  
C) Probe temperature (deg.  
C) Ambient temperature (deg.  
C) Atmospheric pressure (mm)  
Source pressure ("Hg)

Absolute source pressure  
 (mm)  
 Sampling rate (liter/min)  
 Sample loop volume (ml)  
 Sample loop temperature  
 (deg. C)  
 Columnar temperature:  
     Initial (deg. C)/time  
 (min)  
     Program rate (deg.  
 C/min)  
     Final (deg. C/time  
 (min)  
     Carrier gas flow rate  
 (ml/min)  
     Detector temperature  
 (deg. C)  
     Injection time (24-hour  
 basis)  
     Chart speed (mm/min)  
     Dilution gas flow rate  
 (ml/min)  
     Dilution Gas used  
 (symbol)  
     Dilution ratio

Figure 18-11. Field analysis data sheets.

## 2. Field Analysis Data - Calibration Gas

Run No.	Time	A X A	Conc. (ppm)
Components	Area Attenuation	Factor	

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

Figure 18-12. Direct interface sampling system.

[SEE FIGURE IN ORIGINAL]

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

[SEE FIGURE IN ORIGINAL]

## GASEOUS ORGANIC SAMPLING AND ANALYSIS CHECK LIST

(Respond with initials or number as appropriate)

Date

1. Presurvey data:
  - A. Grab sample collected square
  - B. Grab sample analyzed  
for composition square
 

Method GC square	square
GC/MS square	square
Other square	square
  - C. GC-FID analysis per-  
formed square
2. Laboratory calibration data:
  - A. Calibration curves pre-  
pared square
 

Number of compo- nents square	square
Number of concen- trations/ component (3 re- quired) square	square
  - B. Audit samples (option-  
al):
 

Analysis complet- ed square	
Verified for con- centration square	
OK obtained for field work square	
3. Sampling procedures:
  - A. Method:
 

Bag sample square	square
Direct interface square	square
Dilution interface square	square
  - B. Number of samples col-  
lected 1square
4. Field analysis:
  - A. Total hydrocarbon  
analysis performed square
  - B. Calibration curve pre-  
pared square
 

Number of compo- nents square	square
Number of concen- trations per com- ponent (3 re- quired) square	square

Figure 18-14. Sampling and analysis check.

Plant

Date

Location

Source sample	Source sample	Source sample
1	2	3

1. General

information:

Source

temperature

(deg. C)

Probe

temperature

(deg. C)

Ambient

temperature

(deg. C)

Atmospheric

pressure

(mm Hg)

Source

pressure

(mm Hg)

Sampling rate

(ml/min)

Sample loop

volume (ml)

Sample loop

temperature

(deg. C)

Sample

collection

time (24-hr

basis)

Column

tempera-

ture:

Initial

(deg. C)

Program

rate (deg. C/

min)

Final (deg. C)

Carrier gas

flow rate

(ml/min)  
Detector  
temperature  
(deg. C)  
Chart speed  
(cm/min)  
Dilution gas  
flow rate  
(ml/min)  
Diluent gas  
used  
(symbol)  
Dilution ratio

Performed by (signature):

Date:

Figure 18-14. Sampling and analysis sheet.

## METHOD 19--DETERMINATION OF SULFUR DIOXIDE REMOVAL EFFICIENCY AND PARTICULATE MATTER, SULFUR DIOXIDE, AND NITROGEN OXIDES EMISSION RATES

### *1. Applicability and Principle*

1.1 Applicability. This method is applicable for (a) determining particulate matter (PM), sulfur dioxide (SO<sub>2</sub>), and nitrogen oxides (NO<sub>x</sub>) emission rates; (b) determining sulfur removal efficiencies of fuel pretreatment and SO<sub>2</sub> control devices; (c) determining overall reduction of potential SO<sub>2</sub> emissions from steam generating units or other sources as specified in applicable regulations; and (d) determining SO<sub>2</sub> rates based on fuel sampling and analysis procedures.

#### 1.2 Principle.

1.2.1 Pollutant emission rates are determined from concentrations of PM, SO<sub>2</sub>, or NO<sub>x</sub>, and oxygen (O<sub>2</sub>) or carbon dioxide (CO<sub>2</sub>) along with F factors (ratios of combustion gas volumes to heat inputs).

1.2.2 An overall SO<sub>2</sub> emission reduction efficiency is computed from the efficiency of fuel pretreatment systems (optional) and the efficiency of SO<sub>2</sub> control devices.

1.2.3 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.

1.2.4 The SO<sub>2</sub> removal efficiency of a control device is determined by measuring the SO<sub>2</sub> rates before and after the control device.

1.2.5 The inlet rates to SO<sub>2</sub> control systems and when SO<sub>2</sub> control systems are not used, SO<sub>2</sub> emission rates to the atmosphere may be determined by fuel sampling and analysis (optional).

### *2. Emission Rates of Particulate Matter, Sulfur Dioxide, and Nitrogen Oxides*

Select from the following sections the applicable procedure to compute the PM, SO<sub>2</sub>, or NO<sub>x</sub> 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 the following table to make the proper conversion:

#### CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/scm	ng/scm	$10^{-9}$
mg/scm	ng/scm	$10^{-6}$
lb/scf	ng/scm	$1.602 \times 10^{13}$
ppm SO <sub>2</sub>	ng/scm	$2.66 \times 10^6$
ppm NO <sub>x</sub>	ng/scm	$1.912 \times 10^6$
ppm SO <sub>2</sub>	lb/scf	$1.660 \times 10^{-7}$
ppm NO <sub>x</sub>	lb/scf	$1.194 \times 10^{-7}$

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<sub>d</sub>) includes all components of combustion less water, the wet F factor (F<sub>w</sub>) includes all components of combustion, and the carbon F factor (F<sub>c</sub>) includes only carbon dioxide.

NOTE: Since F<sub>w</sub> factors include water resulting only from the combustion of hydrogen in the fuel, the procedures using F<sub>w</sub> 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)

2.1 Oxygen-Based F Factor, Dry Basis. When measurements are on a dry basis for both O<sub>2</sub> (%O<sub>2d</sub>) and pollutant (C<sub>d</sub>) concentrations, use the following equation:

$$E = C[d] \times F[d] \left[ \frac{20.9}{(20.9 - \%O[2d])} \right]$$

Eq. 19-1

2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O<sub>2</sub> (%O<sub>2w</sub>) and pollutant (C<sub>w</sub>) concentrations, use either of the following:

2.2.1 If the moisture fraction of ambient air (B<sub>wa</sub>) is measured:

$$E = [C[w] \times F[w] \times 20.9] / [20.9 \times (1 - B[wa]) - \%O[2w]]$$

Eq. 19-2

Instead of actual measurement, B<sub>wa</sub> 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, of as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture):

2.2.1.1 B<sub>wa</sub> = 0.027. This value may be used at any location at all times.

2.2.1.2 B<sub>wa</sub> = Highest monthly average of B<sub>wa</sub> 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.

2.2.1.3 B[wa] = Highest daily average of B[wa] 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.

2.2.2 If the moisture fraction (B[wa]) of the effluent gas is measured:

$$E = C[w] \times F[d] \left[ \frac{20.9}{20.9 \times (1 - B[wa]) - \%O[2w]} \right]$$

Eq. 19-3

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

2.3.1 When the pollutant concentration is measured on a wet basis (C[w]) and O<sub>2</sub> concentration is measured on a dry basis (%O<sub>2d</sub>), use the following equation:

$$E = \left[ \frac{C[w] \times F[d]}{1 - B[wa]} \right] \left[ \frac{20.9}{20.9 - \%O[2d]} \right]$$

Eq. 19-4

2.3.2 When the pollutant concentration is measured on a dry basis (C[d]) and the O<sub>2</sub> concentration is measured on a wet basis (%O<sub>2w</sub>), use the following equation:

$$E = \frac{C[d] \times F[d] \times 20.9}{20.9 - \%O[2w] \times (1 - B[wa])}$$

Eq. 19-5

2.4 Carbon Dioxide-Based F Factor, Dry Basis. When measurements are on a dry basis for both CO<sub>2</sub> (%CO<sub>2d</sub>) and pollutant (C[d]) concentrations, use the following equation:

$$E = C[d] \times F[c] \times \left( \frac{100}{\%CO[2d]} \right)$$

Eq. 19-6

2.5 Carbon Dioxide-Based F Factor, Wet Basis. When measurements are on a wet basis for both CO<sub>2</sub> (%CO<sub>2w</sub>) and pollutant (C[w]) concentrations, use the following equation:

$$E = C[w] \times F[c] \times \left( \frac{100}{\%CO[2w]} \right)$$

Eq. 19-7

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

2.6.1 When the pollutant concentration is measured on a wet basis (C[w]) and CO<sub>2</sub> concentration is measured on a dry basis (%CO<sub>2d</sub>), use the following equation:

$$E = \left[ \frac{C[w] \times F[c]}{1 - B[wa]} \right] \times \left( \frac{100}{\%CO[2d]} \right)$$

Eq. 19-8

2.6.2 When the pollutant concentration is measured on a dry basis (C[d]) and CO<sub>2</sub> concentration is measured on a wet basis (%CO<sub>2w</sub>), use the following equation:

$$E = C[d] \times (1 - B[wa]) \times F[c] \times (100 / \%CO[2w])$$

Eq. 19-9

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.

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<sub>2</sub> emissions as follows:

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

$$E[bo] = E[co] + (H[g] / H[b]) \times (E[co] - E[g])$$

Eq. 19-10

where:

E[bo] = pollutant emission rate from the steam generating unit, ng/J (lb/million Btu).

E[co] = pollutant emission rate in combined effluent, ng/J (lb/million Btu).

E[g] = pollutant rate from gas turbine, ng/J (lb/million Btu).

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).

2.8.1.1 Use the test methods and procedures section of 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<sub>2</sub> control device is used, measure E[co] after the control device.

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]).

2.8.2 If a control device is used, compute the percent of potential SO<sub>2</sub> emissions (%P[s]) using the following equations:

$$E[bi] = E[ci] - (H[g] / H[b]) \times (E[ci] - E[g])$$

Eq. 19-11

$$\%P[s] = 100 \times (1 - E[bo] / E[bi])$$

Eq. 19-12

where:

E[bi] = pollutant rate from the steam generating unit, ng/J (lb/million Btu)

E[ci] = pollutant rate in combined effluent, ng/J (lb/million Btu).

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].

### 3. F Factors

Use an average F factor according to Section 3.1 or determine an applicable F factor according to Section 3.2. If combined fuels are fired, prorate the applicable F factors using the procedure in Section 3.3.

3.1 Average F Factors. Average F factors (F[d], F[w], or F[c]) from Table 19-1 may be used.

TABLE 19-1--F FACTORS FOR VARIOUS FUELS n1

Fuel type	F[d]		F[w]	
	dscf/10<6>		wscf/10<6>	
	dscm/J	Btu	wscm/J	Btu
Coal:				
Anthracite n2	2.71 X 10<-7>	10,100	2.83 X 10<-7>	10,540
Bituminous n2	2.63 X 10<-7>	9,780	2.86 X 10<-7>	10,640
Lignite	2.65 X 10<-7>	9,860	3.21 X 10<-7>	11,950
Oil n3	2.47 X 10<-7>	9,190	2.77 X 10<-7>	10,320
Gas:				
Natural	2.43 X 10<-7>	8,710	2.85 X 10<-7>	10,610
Propane	2.34 X 10<-7>	8,710	2.74 X 10<-7>	10,200
Butane	2.34 X 10<-7>	8,710	2.79 X 10<-7>	10,390
Wood	2.48 X 10<-7>	9,240		
Wood Bark	2.58 X 10<-7>	9,600		
Municipal Solid Waste	2.57 X 10<-7>	9,570		

Fuel type	scm/J	F[c]	
		scf/10<6>	Btu
Coal:			
Anthracite n2	0.530 X 10<-7>		1,970
Bituminous n2	0.484 X 10<-7>		1,800
Lignite	0.513 X		1,910

	10<-7>	
	0.383 X	
Oil n3	10<-7>	1,420
Gas		
	0.287 X	
Natural	10<-7>	1,040
	0.321 X	
Propane	10<-7>	1,190
	0.337 X	
Butane	10<-7>	1,250
	0.492 X	
Wood	10<-7>	1,830
	0.516 X	
Wood Bark	10<-7>	1,920
	0.488 X	
Municipal	10<-7>	1,820
Solid Waste		

n1 Determined at standard conditions: 20 deg. C (68 deg. F) and 760 mm Hg (29.92 in. Hg).

n2 As classified according to ASTM D388-77.

n3 Crude, residual, or distillate.

3.2 Determined F Factors. If the fuel burned is not listed in Table 19-1 or if the owner or operator chooses to determine an F factor rather than use the values in Table 19-1, use the procedure below:

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

$$F[d] = K \times [(K[hd]\%H) + (K[c]\%C) + (K[s]\%S) + (K[n]\%N) - (K[o]\%O)] / GCV$$

Eq. 19-13

$$F[w] = K \times [(K[hw]\%H) + (K[c]\%C) + (K[s]\%S) + (K[n]\%N) - (K[o]\%O) + (K[w]\%H[2]O)] / GCV[w]$$

Eq. 19-14

$$F[c] = K \times (K[cc]\%C) / GCV$$

Eq. 19-15

(NOTE.--Omit the %H[2]O term in the equations for F[w] if %H and %O include the unavailable hydrogen and oxygen in the form of H[2]O.)

where:

F[d],F[w],F[c] = volumes of combustion components per unit of heat content, scm/J (scf/million Btu).

%H, %C, %S, %N, %O, and %H[2]O = concentrations of hydrogen, carbon, sulfur, nitrogen, oxygen, and water from an ultimate analysis of fuel, weight percent.

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

K = conversion factor, 10<sup>-5</sup> (kJ/J)/(%) [10<sup>6</sup> Btu/million Btu].

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

$K_c = 9.57 \text{ (scm/kg)} [(1.53 \text{ (scf/lb)})/(\%)]$ .

$K_s = 3.54 \text{ (scm/kg)} [(0.57 \text{ (scf/lb)})/(\%)]$ .

$K_n = 0.86 \text{ (scm/kg)} [0.14 \text{ (scf/lb)}/(\%)]$ .

$K_o = 2.85 \text{ (scm/kg)} [0.46 \text{ (scf/lb)}/(\%)]$ .

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

$K_w = 1.30 \text{ (scm/kg)} [(0.21 \text{ (scf/lb)})/(\%)]$ .

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

3.2.2 Use applicable sampling procedures in Section 5.2.1 or 5.2.2 to obtain samples for analyses.

3.2.3 Use ASTM D3176-74 (incorporated by reference--see § 60.17) for ultimate analysis of the fuel.

3.2.4 Use applicable methods in Section 5.2.1 or 5.2.2 to determine the heat content of solid or liquid fuels. For gaseous fuels, use ASTM D1826-77 (IBR--see § 60.17) to determine the heat content.

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

$$F_d = \sum_{k=1}^n X_k F_{dk}$$

Eq. 19-16

$$F_w = \sum_{k=1}^n X_k F_{wk}$$

Eq. 19-17

$$F_c = \sum_{k=1}^n X_k F_{ck}$$

Eq. 19-18

where:

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

n = number of fuels being burned in combination.

#### 4. Determination of Average Pollutant Rates

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:

$$E[a] = (1 / H) \times \sum_{j=1}^n E[h_j]$$

Eq. 19-19

where:

E [a] = average pollutant rate for the specified performance test period, ng/J (lb/million Btu).

E[h] = hourly average pollutant, ng/J (lb/million Btu).

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

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:

$$E[a] = \frac{\sum_{j=1}^D (n[d_j] \times E[d_j])}{\sum_{j=1}^D n[d_j]}$$

Eq. 19-20

where:

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).

n[d] = number of operating hours of the affected facility within the performance test period for each E[d] determined.

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

4.3 Daily Geometric Average Pollutant Rates from Hourly Values. The geometric average pollutant rate (E[ga]) is computed using the following equation:

$$E[ga] = \text{EXP} \left[ \frac{1}{n} \times \sum_{j=1}^n \ln(E[h_j]) \right]$$

Eq. 19-20a

where:

E[ga] = daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O<sub>2</sub>.

E[h<sub>j</sub>] = hourly arithmetic average pollutant rate for hour "j," ng/J (lb/million Btu) or ppm corrected to 7 percent O<sub>2</sub>.

n = total number of hourly averages for which pollutant rates are available within the 24 hr midnight to midnight daily period.

ln = natural log of indicated value.

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

## 5. Determination of Overall Reduction in Potential Sulfur Dioxide Emission

5.1 Overall Percent Reduction. Compute the overall percent SO<sub>2</sub> reduction (%R<sub>[o]</sub>) using the following equation:

$$\%R[o] = 100 \times [1.0 - (1.0 - \%R[f] / 100) \times (1.0 - R[g] / 100)]$$

Eq. 19-21

where:

%R<sub>[f]</sub> = SO<sub>2</sub> removal efficiency from fuel pretreatment, percent.

%R<sub>[g]</sub> = SO<sub>2</sub> removal efficiency of the control device, percent.

5.2 Pretreatment Removal Efficiency (Optional). Compute the SO<sub>2</sub> removal efficiency from fuel pretreatment (%R<sub>[f]</sub>) for the averaging period (e.g., 90 days) as specified in the applicable regulation using the following equation:

$$\%R[f] = 100 \times (1.0 - [\text{<n> SIGMA } [j = 1] \times (\%S[p_j] / \text{GCV}[p_j]) \times L[p_j] / [\text{<n> SIGMA } [j = 1] \times (\%S[r_j] / \text{GCV}[r_j]) \times L[r_j]])$$

Eq. 19-22

where:

%S<sub>[p]</sub>, %S<sub>[r]</sub> = sulfur content of the product and raw fuel lots, respectively, dry basis weight percent.

GCV<sub>[p]</sub>, GCV<sub>[r]</sub> = gross calorific value for the product and raw fuel lots, respectively, dry basis, kg/kg (Btu/lb).

L<sub>[p]</sub>, L<sub>[r]</sub> = weight of the product and raw fuel lots, respectively, metric ton (ton).

n = number of fuel lots during the averaging period.

NOTE: In calculating %R<sub>[f]</sub>, include %S and GCV values for all fuel lots that are not pretreated and are used during the averaging period.

### 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.

5.2.1.1 Sample Increment Collection. Use ASTM D2234-76 (IBR - 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 D2234-76. Collect one gross sample for each lot of raw coal and one gross sample for each lot of product coal.

5.2.1.2 ASTM Lot Size. For the purpose of Section 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.

5.2.1.3 Gross Sample Analysis. Use ASTM D2013-72 to prepare the sample, ASTM D3177-75 or ASTM D4239-85 to determine sulfur content (%S), ASTM D3173-73 to determine moisture content, and ASTM D2015-77 or ASTM D3286-85 to determine gross calorific value (GCV) (all methods cited IBR -- see § 60.17) on a dry basis for each gross sample.

5.2.2 Liquid Fossil Fuel -- Sampling and Analysis. See NOTE under Section 5.2.1.

5.2.2.1 Sample Collection. Follow the procedures for continuous sampling in ASTM D270-65 (Reapproved 1975) (IBR -- see § 60.17) for each gross sample from each fuel lot.

5.2.2.2 Lot Size. For the purpose of Section 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.

5.2.2.3 Sample Analysis. Use ASTM D129-64 (Reapproved 1978), ASTM D1552-83, or ASTM D4057-81 to determine the sulfur content (%S) and ASTM D240-76 (all methods cited IBR -- 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.

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.

5.3 Control Device Removal Efficiency. Compute the percent removal efficiency (%R[g]) of the control device using the following equation:

$$\%R[g] = 100 [1.0 - E[ao] / E[ai]]$$

Eq. 19-23

where:

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).

5.3.1 Use continuous emission monitoring systems or test methods, as appropriate, to determine the outlet SO<sub>2</sub> rates and, if appropriate, the inlet SO<sub>2</sub> 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 4.

5.3.2 As an alternative, as-fired fuel sampling and analysis may be used to determine inlet SO<sub>2</sub> rates as follows:

5.3.2.1 Compute the average inlet SO<sub>2</sub> rate (E[di]) for each sampling period using the following equation:

$$E[di] = K (\%S / GCV)$$

Eq. 19-24

where:

E[di] = average inlet SO<sub>2</sub> rate for each sampling period d, ng / J (lb/million Btu)

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

GCV = gross calorific value of the fuel lot consistent with the sulfur analysis, kJ / kg (Btu/lb).

$$K = 2 \times 10^7 \times [(kg)(ng) / (\%)(J)] \times [2 \times 10^4 (lb)(Btu / (\%)) (\text{million Btu})]$$

After calculating E[di] use the procedures in Section 4.2 to determine the average inlet SO<sub>2</sub> rate for the performance test period (E [ai]).

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 5.3.2 or Section 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.

5.3.2.3 Use ASTM procedures specified in Section 5.2.1 or 5.2.2 to determine the sulfur contents (%S) and gross calorific values (GCV).

5.4 Daily Geometric Average Percent Reduction from Hourly Values. The geometric average percent reduction (%R[ga]) is computed using the following equation:

$$\%R[ga] = 100 [1 - \text{EXP}[(1 / n) \times \sum_{j=1}^n \ln(E[jo] / E[ji])]]$$

Eq. 19-24a

where:

%R[ga] = daily geometric average percent reduction.

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<sub>2</sub>.

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

ln = natural log of indicated value.

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

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

### 6. Sulfur Retention Credit for Compliance Fuel

If fuel sampling and analysis procedures in Section 5.2.1 are being used to determine average SO<sub>2</sub> emission rates (E[as]) to the atmosphere from a coal-fired steam generating unit when there is no SO<sub>2</sub> 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:

$$E[di] = 0.97 K (\%S / GCV)$$

Eq. 19-25

E[di] = average inlet SO<sub>2</sub> rate for each sampling period d, ng/J (lb/million Btu)

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

GCV = gross calorific value of the fuel lot consistent with the sulfur analysis, kg/kg (Btu/lb).

$$K = 2 \times 10^7 \times [(kg)(ng) / (\%)(J)] \times [2 \times 10^4 \times (lb)(Btu / (\%))(million Btu)]$$

After calculating E [di] use the procedures in Section 4-2 to determine the average SO<sub>2</sub> emission rate to the atmosphere for the performance test period (E[ao]).

### 7. Determination of Compliance When Minimum Data Requirement Is Not Met

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.

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:

$$E[ao] * = E[ao] - t[0.95] S[o]$$

Eq. 19-26

where:

S[o] = standard deviation of the hourly average emission rates for each performance test period, ng/J (lb/million Btu).

t[0.95] = values shown in Table 19-2 for the indicated number of data points n.

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:

$$\%R[g] = 100 \times [1.0 - E[ao] * / E[ai] *]$$

Eq. 19-27

$$E[ai] * = E[ai] + t[0.95] S[i]$$

Eq. 19-28

where:

S[1] = standard deviation of the hourly average inlet pollutant rates for each performance test period, ng/J (lb/million Btu).

TABLE 19-2 -- VALUES FOR T[0.95]

n	n1	t[0.95]	n	n1	t[0.95]	n	n1	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	59-91		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

n1 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.

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:

$$S[e] = \sqrt{\frac{1}{H} - \frac{1}{H[r]} \times \left[ \sqrt{\sum_{j=1}^H (E[h_j] - E[a])^2} \right] / (H - 1)}$$

Eq. 19-29

where:

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

$H[r]$  = total numbers of hours in the performance test period (e.g., 720 hours for 30-day performance test period).

Equation 19-29 may be used to compute the standard deviation for both the outlet ( $S[o]$ ) and, if applicable, inlet ( $S[i]$ ) pollutant rates.

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

### 1. *Principle and Applicability*

1.1 Applicability. This method is applicable for the determination of nitrogen oxides ( $NO[x]$ ), sulfur dioxide ( $SO[2]$ ), and a diluent gas, either oxygen ( $O[2]$ ) or carbon dioxide ( $CO[2]$ ), emissions from stationary gas turbines. For the  $NO[x]$  and diluent concentration determinations, this method includes: (1) Measurement system design criteria; (2) Analyzer performance specifications and performance test procedures; and (3) Procedures for emission testing.

1.2 Principle. A gas sample is continuously extracted from the exhaust stream of a stationary gas turbine; a portion of the sample stream is conveyed to instrumental analyzers for determination of  $NO[x]$  and diluent content. During each  $NO[x]$  and diluent determination, a separate measurement of  $SO[2]$  emissions is made, using Method 6, or its equivalent. The diluent determination is used to adjust the  $NO[x]$  and  $SO[2]$  concentrations to a reference condition.

### 2. *Definitions*

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

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

2.1.2  $NO[x]$  Analyzer. That portion of the system that senses  $NO[x]$  and generates an output proportional to the gas concentration.

2.1.3  $O[2]$  Analyzer. That portion of the system that senses  $O[2]$  and generates an output proportional to the gas concentration.

2.1.4  $CO[2]$  Analyzer. That portion of the system that senses  $CO[2]$  and generates an output proportional to the gas concentration.

2.1.5 Data Recorder. That portion of the measurement system that provides a permanent record of the analyzer(s) output. The data recorder may include automatic data reduction capabilities.

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

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

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

2.5 Zero Drift. The difference in the measurement system output readings from zero after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place and the input concentration at the time of the measurements was zero.

2.6 Calibration Drift. The difference in the measurement system output readings from the known concentration of the calibration gas after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place and the input at the time of the measurements was a high-level value.

2.7 Response Time. The amount of time required for the measurement system to display on the data output 95 percent of a step change in pollutant concentration.

2.8 Interference Response. The output response of the measurement system to a component in the sample gas, other than the gas component being measured.

### 3. *Measurement System Performance Specifications*

3.1 NO<sub>2</sub> to NO Converter. Greater than 90 percent conversion efficiency of NO<sub>2</sub> to NO.

3.2 Interference Response. Less than +/- 2 percent of the span value.

3.3 Response Time. No greater than 30 seconds.

3.4 Zero Drift. Less than +/- 2 percent of the span value over the period of each test run.

3.5 Calibration Drift. Less than +/- 2 percent of the span value over the period of each test run.

### 4. *Apparatus and Reagents*

4.1 Measurement System. Use any measurement system for NO<sub>x</sub> and diluent that is expected to meet the specifications in this method. A schematic of an acceptable measurement system is shown in Figure 20-1. The essential components of the measurement system are described below:

Figure 20.1 Measurement system design.

[SEE FIGURE IN ORIGINAL]

4.1.1 Sample Probe. Heated stainless steel, or equivalent, open-ended, straight tube of sufficient length to traverse the sample points.

4.1.2 Sample Line. Heated (> 95 deg. C) stainless steel or Teflon tubing to transport the sample gas to the sample conditioners and analyzers.

4.1.3 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the sample conditioners and to the analyzers. The calibration valve assembly shall be capable of blocking the sample gas flow and of introducing calibration gases to the measurement system when in the calibration mode.

4.1.4 NO<sub>2</sub> to NO Converter. That portion of the system that converts the nitrogen dioxide (NO<sub>2</sub>) in the sample gas to nitrogen oxide (NO). Some analyzers are designed to measure NO<sub>x</sub> as NO<sub>2</sub> on a wet basis and can be used without an NO<sub>2</sub> to NO converter or a moisture removal trap provided the sample line to the analyzer is heated (> 95 deg. C) to the inlet of the analyzer. In addition, an NO<sub>2</sub> to NO converter is not necessary if the NO<sub>2</sub> portion of the exhaust gas is less than 5 percent of the total NO<sub>x</sub> concentration. As a guideline, an NO<sub>2</sub> to NO converter is not necessary if the gas turbine is operated at 90 percent or more of peak

load capacity. A converter is necessary under lower load conditions.

4.1.5 Moisture Removal Trap. A refrigerator-type condenser or other type device designed to continuously remove condensate from the sample gas while maintaining minimal contact between any condensate and the sample gas. The moisture removal trap is not necessary for analyzers that can measure NO[x] concentrations on a wet basis; for these analyzers, (a) heat the sample line up to the inlet of the analyzers, (b) determine the moisture content using methods subject to the approval of the Administrator, and (c) correct the NO[x] and diluent concentrations to a dry basis.

4.1.6 Particulate Filter. An in-stack or an out-of-stack glass fiber filter, of the type specified in EPA Method 5; however, an out-of-stack filter is recommended when the stack gas temperature exceeds 250 to 300 deg. C.

4.1.7 Sample Pump. A nonreactive leakfree sample pump to pull the sample gas through the system at a flow rate sufficient to minimize transport delay. The pump shall be made from stainless steel or coated with Teflon or equivalent.

4.1.8 Sample Gas Manifold. A sample gas manifold to divert portions of the sample gas stream to the analyzers. The manifold may be constructed of glass, Teflon, stainless steel, or equivalent.

4.1.9 Diluent Gas Analyzer. An analyzer to determine the percent O<sub>2</sub> or CO<sub>2</sub> concentration of the sample gas.

4.1.10 Nitrogen Oxides Analyzer. An analyzer to determine the ppm NO[x] concentration in the sample gas stream.

4.1.11 Data Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data.

4.2 Sulfur Dioxide Analysis. EPA Method 6 apparatus and reagents.

4.3 NO[x] Calibration Gases. The calibration gases for the NO[x] analyzer shall be NO in N<sub>2</sub>. Use four calibration gas mixtures as specified below:

4.3.1 High-level Gas. A gas concentration that is equivalent to 80 to 90 percent of the span value.

4.3.2 Mid-level Gas. A gas concentration that is equivalent to 45 to 55 percent of the span value.

4.3.3 Low-level Gas. A gas concentration that is equivalent to 20 to 30 percent of the span value.

4.3.4 Zero Gas. A gas concentration of less than 0.25 percent of the span value. Ambient air may be used for the NO[x] zero gas.

4.4 Diluent Calibration Gases.

4.4.1 For O<sub>2</sub> calibration gases, use purified air at 20.9 percent O<sub>2</sub> as the high-level O<sub>2</sub> gas. Use a gas concentration between 11 and 15 percent O<sub>2</sub> in nitrogen for the mid-level gas, and use purified nitrogen for the zero gas.

4.4.2 For CO<sub>2</sub> calibration gases, use a gas concentration between 8 and 12 percent CO<sub>2</sub> in air for the high-level calibration gas. Use a gas concentration between 2 and 5 percent CO<sub>2</sub> in air for the mid-level calibration gas, and use purified air (< 100 ppm CO<sub>2</sub>) as the zero level calibration gas.

## 5. Measurement System Performance Test Procedures

Perform the following procedures prior to measurement of emissions (Section 6) and only once for each test program, i.e., the series of all test runs for a given gas turbine engine.

5.1 Calibration Gas Checks. There are two alternatives for checking the concentrations of the calibration gases. (a) The first is to use calibration gases that are documented traceable to National Bureau of Standards Reference Materials. Use *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors* (Protocol Number 1) that is available from the Environmental Monitoring Systems Laboratory, Quality Assurance Branch, Mail Drop 77, Environmental Protection Agency, Research Triangle Park, NC 27711. Obtain a certification from the gas manufacturer that the protocol was followed. These calibration gases are not to be analyzed with the Reference Methods. (b) The second alternative is to use calibration gases not prepared according to the protocol. If this alternative is chosen, within 1 month prior to the emission test, analyze each of the calibration gas mixtures in triplicate using Method 7 or the procedure outlined in Citation 1 for NO[x] and use Method 3 for O[2] or CO[2]. Record the results on a data sheet (example is shown in Figure 20-2). For the low-level, mid-level, or high-level gas mixtures, each of the individual NO[x] analytical results must be within 10 percent (or 10 ppm, whichever is greater) of the triplicate set average (O[2] or CO[2] test results must be within 0.5 percent O[2] or CO[2]); otherwise, discard the entire set and repeat the triplicate analyses. If the average of the triplicate reference method test results is within 5 percent for NO[x] gas or 0.5 percent O[2] or CO[2] for the O[2] or CO[2] gas of the calibration gas manufacturer's tag value, use the tag value; otherwise, conduct at least three additional reference method test analyses until the results of six individual NO[x] runs (the three original plus three additional) agree within 10 percent (or 10 ppm, whichever is greater) of the average (O[2] or CO[2] test results must be within 0.5 percent O[2] or CO[2]). Then use this average for the cylinder value.

5.2 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing and operating the NO[2] to NO converter, the NO[x] analyzer, the diluent analyzer, and other components.

FIGURE 20-2 -- ANALYSIS OF CALIBRATION GASES

Date (Must be within 1 month prior to the test period)

Reference method used

Sample run	Gas concentration, ppm		
	Low level a	Mid level b	High level c
1			
2			
3			
Average			
Maximum % deviation d			

a Average must be 20 to 30% of span value.

b Average must be 45 to 55% of span value.



c Average must be 80 to 90% of span value.

d Must be  $\leq \pm 10\%$  of applicable average or 10 ppm, whichever is greater.

FIGURE 20-3 -- ZERO AND CALIBRATION DATA

Turbine type	Identification number
Date	Test number
Analyzer type	Identification number

	Cylinder value, ppm or %	Initial analyzer response, ppm or %	Final analyzer responses, ppm or %
Zero gas			
Low-level gas			
Mid-level gas			
High-level gas			

**Difference: initial-  
final,  
ppm or %**

Zero gas
Low-level gas
Mid-level gas
High-level gas

5.3 Calibration Check. Conduct the calibration checks for both the NO[x] and the diluent analyzers as follows:

5.3.1 After the measurement system has been prepared for use (Section 5.2), introduce zero gases and the mid-level calibration gases; set the analyzer output responses to the appropriate levels. Then introduce each of the remainder of the calibration gases described in Sections 4.3 or 4.4, one at a time, to the measurement system. Record the responses on a form similar to Figure 20-3.

5.3.2 If the linear curve determined from the zero and mid-level calibration gas responses does not predict the actual response of the low-level (not applicable for the diluent analyzer) and high-level gases within 2 percent of the span value, the calibration shall be considered invalid. Take corrective measures on the measurement system before proceeding with the test.

5.4 Interference Response. Introduce the gaseous components listed in Table 20-1 into the measurement system

separately, or as gas mixtures. Determine the total interference output response of the system to these components in concentration units; record the values on a form similar to Figure 20-4. If the sum of the interference responses of the test gases for either the NO[x] or diluent analyzers is greater than 2 percent of the applicable span value, take corrective measure on the measurement system.

$$\text{Percent drift} = \text{Absolute difference} / \text{Span value} \times 100$$

TABLE 20-1 -- INTERFERENCE TEST GAS CONCENTRATION

CO	500 +/- 50 ppm	CO[2]	10 +/- 1 percent.
SO[2]	200 +/- 20 ppm	O[2]	20.9 +/- 1 percent.

FIGURE 20-4 -- INTERFERENCE RESPONSE

Date of test

Analyzer type

Serial No.

Test gas type	Concentration, ppm	Analyzer output response	% of span
---------------------	-----------------------	--------------------------------	--------------

$$\% \text{ of span} = \text{Analyzer output response} / \text{Instrument span} \times 100$$

Conduct an interference response test of each analyzer prior to its initial use in the field. Thereafter, recheck the measurement system if changes are made in the instrumentation that could alter the interference response, e.g., changes in the type of gas detector.

In lieu of conducting the interference response test, instrument vendor data, which demonstrate that for the test gases of Table 20-1 the interference performance specification is not exceeded, are acceptable.

5.5 Response Time. To determine response time, first introduce zero gas into the system at the calibration valve until all readings are stable; then, switch to monitor the stack effluent until a stable reading can be obtained. Record the upscale response time. Next, introduce high-level calibration gas into the system. Once the system has stabilized at the high-level concentration, switch to monitor the stack effluent and wait until a stable value is reached. Record the downscale response time. Repeat the procedure three times. A stable value is equivalent to a change of less than 1 percent of span value for 30 seconds or less than 5 percent of the measured average concentration for 2 minutes. Record the response time data on a form similar to Figure 20-5, the readings of the upscale or downscale response time, and report the greater time as the "response time" for the analyzer. Conduct a response time test prior to the initial field use of the measurement system, and repeat if changes are made in the measurement system.

FIGURE 20-5 -- RESPONSE TIME

Date of test

Analyzer type

S/N

Span gas concentration: ppm.

Analyzer span setting: ppm.

Upscale:

1 seconds.

2 seconds.

3 seconds.

Average upscale response seconds.

Downscale:

1 seconds.

2 seconds.

3 seconds.

Average downscale response seconds.

System response time=

slower average time=

seconds.

## 5.6 NO<sub>2</sub> to NO Conversion Efficiency.

5.6.1 Add gas from the mid-level NO in N<sub>2</sub> calibration gas cylinder to a clean, evacuated, leak-tight Tedlar bag. Dilute this gas approximately 1:1 with 20.9 percent O<sub>2</sub> purified air. Immediately attach the bag outlet to the calibration valve assembly and begin operation of the sampling system. Operate the sampling system, recording the NO<sub>x</sub> response, for at least 30 minutes. If the NO<sub>2</sub> to NO conversion is 100 percent, the instrument response will be stable at the highest peak value observed. If the response at the end of 30 minutes decreases more than 2.0 percent of the highest peak value, the system is not acceptable and corrections must be made before repeating the check.

5.6.2 Alternatively, the NO<sub>2</sub> to NO converter check described in Title 40, Part 86: Certification and Test Procedures for Heavy-duty Engines for 1979 and Later Model Years may be used. Other alternative procedures may be used with approval of the Administrator.

## 6. Emission Measurement Test Procedure

## 6.1 Preliminaries.

6.1.1 Selection of a Sampling Site. Select a sampling site as close as practical to the exhaust of the turbine. Turbine geometry, stack configuration, internal baffling, and point of introduction of dilution air will vary for different turbine designs. Thus, each of these factors must be given special consideration in order to obtain a representative sample. Whenever possible, the sampling site shall be located upstream of the point of introduction of dilution air into the duct. Sample ports may be located before or after the upturn elbow, in order to accommodate the configuration of the turning vanes and baffles and to permit a complete, unobstructed traverse of the stack. The sample ports shall not be located within 5 feet or 2 diameters (whichever is less) of the gas discharge to atmosphere. For supplementary-fired, combined-cycle plants, the sampling site shall be located between the gas turbine and the boiler. The diameter of the sample ports shall be sufficient to allow entry of the sample probe.

6.1.2 A preliminary O<sub>2</sub> or CO<sub>2</sub> traverse is made for the purpose of selecting sampling points of low O<sub>2</sub> or high CO<sub>2</sub> concentrations, as appropriate for the measurement system. Conduct this test at the turbine operating condition that is the lowest percentage of peak load operation included in the test program. Follow the procedure below, or use an alternative procedure subject to the approval of the Administrator.

6.1.2.1 Minimum Number of Points. Select a minimum number of points as follows: (1) Eight, for stacks having cross-sectional areas less than 1.5 m<sup>2</sup> (16.1 ft<sup>2</sup>); (2) eight plus one additional sample point for each 0.2 m<sup>2</sup> (2.2 ft<sup>2</sup>) of areas, for stacks of 1.5 m<sup>2</sup> to 10.0 m<sup>2</sup> (16.1-107.6 ft<sup>2</sup>) in cross-sectional area; and (3) 49 sample points (48 for circular stacks) for stacks greater than 10.0 m<sup>2</sup> (107.6 ft<sup>2</sup>) in cross-sectional area. Note that for circular ducts, the number of sample points must be a multiple of 4, and for rectangular ducts, the number of points must be one of those listed in Table 20-2; therefore, round off the number of points (upward), when appropriate.

6.1.2.2 Cross-sectional Layout and Location of Traverse Points. After the number of traverse points for the preliminary diluent sampling has been determined, use Method 1 to located the traverse points.

6.1.2.3 Preliminary Diluent Measurement. While the gas turbine is operating at the lowest percent of peak load, conduct a preliminary diluent measurement as follows: Position the probe at the first traverse point and begin sampling. The minimum sampling time at each point shall be 1 minute plus the average system response time. Determine the average steady-state concentration of diluent at each point and record the data on Figure 20-6.

6.1.2.4 Selection of Emission Test Sampling Points. Select the eight sampling points at which the lowest O<sub>2</sub> concentrations or highest CO<sub>2</sub> concentrations were obtained. Sample at each of these selected points during each run at the different turbine load conditions. More than eight points may be used, if desired, providing that the points selected as described above are included.

TABLE 20-2 -- CROSS-SECTIONAL LAYOUT FOR RECTANGULAR STACKS

	<b>Matrix layout</b>
No. of traverse points:	
9	3 x 3
12	4 x 3
16	4 x 4
20	5 x 4
25	5 x 5

30	6 x 5
36	6 x 6
42	7 x 6
49	7 x 7

FIGURE 20-6 -- PRELIMINARY DILUENT TRAVERSE

Date

Location:

Plant

City, State

Turbine identification:

Manufacturer

Model, serial number

Sample point	Diluent concentration, ppm
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6.2 NO[x] and Diluent Measurement. This test is to be conducted at each of the specified load conditions. Three test runs at each load condition constitute a complete test.

6.2.1 At the beginning of each NO[x] test run and, as applicable, during the run, record turbine data as indicated in Figure 20-7. Also, record the location and number of the traverse points on a diagram.

6.2.2 Position the probe at the first point determined in the preceding section and begin sampling. The minimum sampling time at each point shall be at least 1 minute plus the average system response time. Determine the average steady-state concentration of diluent and NO[x] at each point and record the data on Figure 20-8.

FIGURE 20-7 -- STATIONARY GAS TURBINE DATA

TURBINE OPERATION RECORD

Test operator Date

Turbine identification:

Type

Serial No.

Location:

Plant

City

Ambient temperature

Ambient humidity

Test time start

Test time finish

Fuel flow rate na

Water or steam flow rate na

Ambient pressure

Ultimate fuel analysis:

C

H

O

N

S

Ash

H<sub>2</sub>O

Trace metals:

Na

Va

K

etc nb

Operating load

a Describe measurement method, i.e., continuous flow meter, start finish volumes, etc.

b i.e., additional elements added for smoke suppression.

FIGURE 20-8 -- STATIONARY GAS TURBINE SAMPLE POINT RECORD

Turbine identification:

Manufacturer

Model, serial No.

Location:

Plant

City, State

Ambient temperature

Ambient pressure

Date

Test time: start

Test time: finish

Test operator name

Diluent instrument type

Serial No

NO[x] instrument type

Serial No.

Sample point	Time, min	Diluent a%	NO[x] a, ppm
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a Average steady-state value from recorder or instrument readout.

6.2.3 After sampling the last point, conclude the test run by recording the final turbine operating parameters and by determining the zero and calibration drift, as follows:

Immediately following the test run at each load condition, or if adjustments are necessary for the measurement system during the tests, reintroduce the zero and mid-level calibration gases as described in Sections 4.3 and 4.4, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after the drift checks are made). Record the analyzers' responses on a form similar to Figure 20-3. If the drift values exceed the specified limits, the test run preceding the check is considered invalid and will be repeated following corrections to the measurement system. Alternatively, recalibrate the measurement system and recalculate the measurement data. Report the test results based on both the initial calibration and the recalibration data.

6.3 SO<sub>2</sub> Measurement. This test is conducted only at the 100 percent peak load condition. Determine SO<sub>2</sub> using Method 6, or equivalent, during the test. Select a minimum of six total points from those required for the

NO<sub>x</sub> measurements; use two points for each sample run. The sample time at each point shall be at least 10 minutes. Average the diluent readings taken during the NO<sub>x</sub> test runs at sample points corresponding to the SO<sub>2</sub> traverse points (see Section 6.2.2) and use this average diluent concentration to correct the integrated SO<sub>2</sub> concentration obtained by Method 6 to 15 percent diluent (see Equation 20-1).

If the applicable regulation allows fuel sampling and analysis for fuel sulfur content to demonstrate compliance with sulfur emission unit, emission sampling with Method 6 is not required, provided the fuel sulfur content meets the limits of the regulation.

## 7. Emission Calculations

7.1 Moisture Correction. Measurement data used in most of these calculations must be on a dry basis. If measurements must be corrected to dry conditions, use the following equation:

$$C [d] = C[w] / 1 - B[ws]$$

Eq. 20-1

where:

C[d] = Pollutant or diluent concentration adjusted to dry conditions, ppm or percent.

C[w] = Pollutant or diluent concentration measured under moist sample conditions, ppm or percent.

B[ws] = Moisture content of sample gas as measured with Method 4, reference method, or other approved method, percent/100.

7.2 CO<sub>2</sub> Correction Factor. If pollutant concentrations are to be corrected to 15 percent O<sub>2</sub> and CO<sub>2</sub> concentration is measured in lieu of O<sub>2</sub> concentration measurement, a CO<sub>2</sub> correction factor is needed. Calculate the CO<sub>2</sub> correction factor as follows:

7.2.1 Calculate the fuel-specific F<sub>o</sub> value for the fuel burned during the test using values obtained from Method 19, Section 5.2, and the following equation.

$$F[o] = 0.209 F[d] / F[c]$$

Eq. 20-2

where:

F<sub>o</sub> = Fuel factor based on the ratio of oxygen volume to the ultimate CO<sub>2</sub> volume produced by the fuel at zero percent excess air, dimensionless.

0.209 = Fraction of air that is oxygen, percent/100.

F<sub>d</sub> = Ratio of the volume of dry effluent gas to the gross calorific value of the fuel from Method 19, dscf/10<sup>6</sup> Btu).

F<sub>c</sub> = Ratio of the volume of carbon dioxide produced to the gross calorific value of the fuel from Method 19, dscf/10<sup>6</sup> Btu).

7.2.2 Calculate the CO<sub>2</sub> correction factor for correcting measurement data to 15 percent oxygen, as follows:



$$X[\text{CO}_2] = 5.9 / F[\text{O}_2]$$

Eq. 20-3

where:

$X[\text{CO}_2]$  =  $\text{CO}_2$  Correction factor, percent.

5.9 = 20.9 percent  $\text{O}_2$  - 15 percent  $\text{O}_2$ , the defined  $\text{O}_2$  correction value, percent.

7.3 Correction of Pollutant Concentrations to 15 percent  $\text{O}_2$ . Calculate the  $\text{NO}_x$  and  $\text{SO}_2$  gas concentrations adjusted to 15 percent  $\text{O}_2$  using Equation 20-4 or 20-5, as appropriate. The correction to 15 percent  $\text{O}_2$  is very sensitive to the accuracy of the  $\text{O}_2$  or  $\text{CO}_2$  concentration measurement. At the level of the analyzer drift specified in Section 3, the  $\text{O}_2$  or  $\text{CO}_2$  correction can exceed 5 percent at the concentration levels expected in gas turbine exhaust gases. Therefore,  $\text{O}_2$  or  $\text{CO}_2$  analyzer stability and careful calibration are necessary.

7.3.1 Correction of Pollutant Concentration Using  $\text{O}_2$  Concentration. Calculate the  $\text{O}_2$  corrected pollutant concentration, as follows:

$$C[\text{adj}] = C[\text{d}] \frac{5.9}{20.9 - \% \text{O}_2}$$

Eq. 20-4

where:

$C[\text{adj}]$  = Pollutant concentration corrected to 15 percent  $\text{O}_2$  ppm.

$C[\text{d}]$  = Pollutant concentration measured, dry basis, ppm.

$\% \text{O}_2$  = Measured  $\text{O}_2$  concentration dry basis, percent.

7.3.2 Correction of Pollutant Concentration Using  $\text{CO}_2$  Concentration. Calculate the  $\text{CO}_2$  corrected pollutant concentration, as follows:

$$C[\text{adj}] = C[\text{d}] X[\text{CO}_2] / \% \text{CO}_2$$

Eq. 20-5

where:

$\% \text{CO}_2$  = Measured  $\text{CO}_2$  concentration measured, dry basis, percent.

7.4 Average Adjusted  $\text{NO}_x$  Concentration. Calculate the average adjusted  $\text{NO}_x$  concentration by summing the adjusted values for each sample point and dividing by the number of points for each run.

7.5  $\text{NO}_x$  and  $\text{SO}_2$  Emission Rate Calculations. The emission rates for  $\text{NO}_x$  and  $\text{SO}_2$  in units of pollutant mass per quantity of heat input can be calculated using the pollutant and diluent concentrations and fuel-specific F-factors based on the fuel combustion characteristics. The measured concentrations of pollutant in units of parts per million by volume (ppm) must be converted to mass per unit volume concentration units for these calculations. Use the following table for such conversions:

## CONVERSION FACTORS FOR CONCENTRATION

From	To	Multiply by
g/sm <sup>3</sup>	ng/sm <sup>3</sup>	10 <sup>9</sup>
mg/sm <sup>3</sup>	ng/sm <sup>3</sup>	10 <sup>6</sup>
lb/scf	ng/sm <sup>3</sup>	1.602 x 10 <sup>13</sup>
ppm (SO <sub>2</sub> )	ng/sm <sup>3</sup>	2.660 x 10 <sup>6</sup>
ppm (NO <sub>x</sub> )	ng/sm <sup>3</sup>	1.912 x 10 <sup>6</sup>
ppm (SO <sub>2</sub> )	lb/scf	1.660 x 10 <sup>-7</sup>
ppm (NO <sub>x</sub> )	lb/scf	1.194 x 10 <sup>-7</sup>

7.5.1 Calculation of Emission Rate Using Oxygen Correction. Both the O<sub>2</sub> concentration and the pollutant concentration must be on a dry basis. Calculate the pollutant emission rate, as follows:

$$E = C[d]F[d] \frac{20.9}{20.9 - \%O_2}$$

Eq. 20-6

where:

E = Mass emission rate of pollutant, ng/J (lb/10<sup>6</sup> Btu).

7.5.2 Calculation of Emission Rate Using Carbon Dioxide Correction. The CO<sub>2</sub> concentration and the pollutant concentration may be on either a dry basis or a wet basis, but both concentrations must be on the same basis for the calculations. Calculate the pollutant emission rate using Equation 20-7 or 20-8:

$$E = C[d]F[c] \frac{100}{\%CO_2}$$

Eq. 20-7

$$E = C[w]F[c] \frac{100}{\%CO_{2w}}$$

Eq. 20-8

where:

C[w] = Pollutant concentration measured on a moist sample basis, ng/sm<sup>3</sup> (lb/scf).

%CO<sub>2w</sub> = Measured CO<sub>2</sub> concentration measured on a moist sample basis, percent.

## 8. Bibliography

1. Curtis, F. A Method for Analyzing NO<sub>x</sub> Cylinder Gases-Specific Ion Electrode Procedure, Monograph available from Emission Measurement Laboratory, ESED, Research Triangle Park, NC 27711, October 1978.

2. Sigsby, John E., F. M. Black, T. A. Bellar, and D. L. Klosterman. Chemiluminescent Method for Analysis of Nitrogen Compounds in Mobile Source Emissions (NO, NO<sub>2</sub>, and NH<sub>3</sub>). "Environmental Science and Technology," 7:51-54. January 1973.

3. Shigehara, R. T., R. M. Neulicht, and W. S. Smith. Validating Orsat Analysis Data from Fossil Fuel-Fired Units. Emission Measurement Branch, Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. June 1975.

## METHOD 21 -- DETERMINATION OF VOLATILE ORGANIC COMPOUNDS LEAKS

### 1. *Applicability and Principle*

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

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

### 2. *Definitions*

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

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

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

2.4 **No Detectable Emission.** Any VOC concentration at a potential leak source (adjusted for local VOC ambient concentration) that is less than a value corresponding to the instrument readability specification of section 3.1.1(c) indicates that a leak is not present.

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

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

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

### 3. Apparatus

#### 3.1 Monitoring Instrument.

##### 3.1.1 Specifications.

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

b. Both the linear response range and the measurable range of the instrument for each of the VOC to be measured, and for the VOC calibration gas that is used for calibration, shall encompass the leak definition concentration specified in the regulation. A dilution probe assembly may be used to bring the VOC concentration within both ranges; however, the specifications for instrument response time and sample probe diameter shall still be met.

c. The scale of the instrument meter shall be readable to  $\pm 2.5$  percent of the specified leak definition concentration when performing a no detectable emission survey.

d. The instrument shall be equipped with an electrically driven pump to insure 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 liters per minute when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

e. The instrument shall be intrinsically safe as defined by the applicable U.S.A. standards (e.g., National Electric Code by the National Fire Prevention Association) 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 Class 2, Division 1 conditions, as defined by the example Code. The instrument shall not be operated with any safety device, such as an exhaust flame arrestor, removed.

f. The instrument shall be equipped with a probe or probe extension for sampling not to exceed 1/4 in. in outside diameter, with a single end opening for admission of sample.

##### 3.1.2 Performance Criteria.

(a) The instrument response factors for each of the VOC to be measured shall be less than 10. 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 VOC to be measured.

(b) 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.

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

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

### 3.1.3 Performance Evaluation Requirements.

- a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.
- b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.
- c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

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

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

## 4. Procedures

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

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

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

### 4.3 Individual Source Surveys.

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

- a. Valves -- The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem 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.
- b. Flanges and Other Connections -- For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.
- c. Pumps and Compressors -- Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.
- d. Pressure Relief Devices -- The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.
- e. Process Drains -- For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.
- f. Open-Ended Lines or Valves -- Place the probe inlet at approximately the center of the opening to the atmosphere.
- g. Seal System Degassing Vents and Accumulator Vents -- Place the probe inlet at approximately the center of the opening to the atmosphere.
- h. Access Door Seals -- Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

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

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

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

- (a) Pump or Compressor Seals -- If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.
- (b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices -- If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there

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

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

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

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

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

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

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

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

## 5. Bibliography

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## METHOD 22 -- VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES

### 1. *Introduction*

This method involves the visual determination of fugitive emissions, i.e., emissions not emitted directly from a process stack or duct. Fugitive emissions include 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; and (4) are emitted directly from process equipment. This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

This method determines the amount of time that any 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 a visible emission occurs and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 are not required. However, it is necessary that the observer is educated on the general procedures for determining the presence of visible emissions. As a minimum, the observer must be trained and knowledgeable regarding the effects on the visibility of emissions caused by background contrast, ambient lighting, observer position relative to lighting, wind, and the presence of uncombined water (condensing water vapor). This training is to be obtained from written materials found in Citations 1 and 2 of Bibliography or from the lecture portion of the Method 9 certification course.

### 2. *Applicability and Principle*

2.1 *Applicability.* This method applies to the determination of the frequency of fugitive emissions from stationary sources (located indoors or outdoors) when specified as the test method for determining compliance with new source performance standards.

This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.2 *Principle.* 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.

### 3. *Definitions*

3.1 *Emission Frequency.* Percentage of time that emissions are visible during the observation period.

3.2 *Emission Time.* Accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive Emissions.* Pollutant generated by an affected facility which is not collected by a capture system and is released to the atmosphere.

3.4 *Smoke Emissions.* 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.

3.5 Observation Period. Accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

#### 4. *Equipment*

4.1 Stopwatches. Accumulative type with unit divisions of at least 0.5 seconds; two required.

4.2 Light Meter. Light meter capable of measuring illuminance in the 50- to 200-lux range; required for indoor observations only.

#### 5. *Procedure*

5.1 Position. Survey the affected facility or 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 15 feet, but not more than 0.25 miles, from the emission source is recommended. For outdoor locations, select a position where the sun is not directly in the observer's eyes.

#### 5.2 Field Records.

5.2.1 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.

5.2.2 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 observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

5.3 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.

5.4 Observations. 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, stop the stopwatch when a break begins and restart it without resetting 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 the 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.

5.4.1 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission regulation in the applicable subpart. 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 observation 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 emissions 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.

5.4.2 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.

5.4.3 Visual Interference. 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 are terminated, and the observer clearly notes this fact on the data form.

5.5 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.

## 6. *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.

## 7. *Bibliography*

1. Missan, Robert and Arnold 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. Guidelines for Development of a Quality Assurance Program: Volume IX -- Visual Determination of Opacity Emissions From Stationary Sources. EPA Publication No. EPA-650/4-74-005-i. November 1975.

Figure 22-1

[SEE FIGURE IN ORIGINAL]

Figure 22-2

[SEE FIGURE IN ORIGINAL]

## 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

[SEE FIGURE IN ORIGINAL]

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 (1/2 in. OD with 1/8 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 deg. 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 deg. C (68 deg. F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic 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

[SEE FIGURE IN ORIGINAL]

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 Metal 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 x 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 +/- deg. C and performing programmed increases in temperature at rates of at least 40 deg. C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures +/- 1 deg. 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 X 0.25 mm inside diameter (ID), coated with DB-5 and a

fused silica column, 30 m X 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<sub>2</sub> 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 deg. 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 to 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  $\mu$ l sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft X 1/8 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  $4 \times 10^{-11}$  A/mV.

Injection Port Temperature: 250 deg. C.

Detector Temperature: 305 deg. C.

Oven Temperature: 30 deg. C for 4 min; programmed to rise at 40 deg. C/min until it reaches 250 deg. C; return to 30 deg. 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  $\mu$ l of methylene chloride into 100 ml of toluene. This corresponds to 100  $\mu$ g of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000  $\mu$ g/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 deg. 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 deg. C (350 deg. 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 quality.

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 deg. 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 deg. C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 deg. C for 10 minutes, then increase the temperature gradually to 180 deg. 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  $\mu$ l 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.

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 deg. C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20 deg. 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  $\pm 1$  ml by using a graduated cylinder or by weighing it to within  $\pm 0.5$  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.

## 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 deg. 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  $\mu$ l 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 2/3 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  $\mu$ l 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 deg. C. Rinse the sample container apparatus at a temperature of less than 37 deg. 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 x 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 bottom 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 deg. C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200  $\mu$ l using a stream of N<sub>2</sub>. 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  $\mu$ l aliquot of the Recovery Standard solution from Table 1 to each sample. A 2  $\mu$ l 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 deg. C.

5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

5.3.1.3 Oven. Initially at 150 deg. C. Raise by at least 40 deg. C/min to 190 deg. C and then at 3 deg. C/min up to 300 deg. 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 deg. 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  $\mu$ l 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  $\mu$ l of the surrogate standards in Table 1 to the adsorbent 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. *Quality Assurance*

8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 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 i 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.

$$RRF[1] = 1 / n \sum_{j=1}^n A[cij]m*[ci] / A*[cij]m[ci]$$

Eq. 23-1 . . .

9.3 Concentration of the PCDD's and PCDF's.

$$C[i] = m[i]*A[i] / A[i]*RRF[i]V[mstd]$$

Eq. 23-2

9.4 Recovery Standard Response Factor.

$$RRF[rs] = A[ci]*m[rs] / A[rs]m[ci]*$$

Eq. 23-3

9.5 Recovery of Internal Standards (R\*).

$$R* = A[i]*m[rs] / A[rs]RF[rs]m[i]* \times 100\%$$

Eq. 23-4

## 9.6 Surrogate Compound Response Factor.

$$\text{RRF}[s] = A[\text{ci}] * m[s] / A[\text{cis}] m[\text{ci}] *$$

Eq. 23-5

## 9.7 Recovery of Surrogate Compounds (R [s]).

$$R[s] = A[s] m[i] * / A[i] * \text{RRF}[s] m[s] \times 100\%$$

Eq. 23-6

## 9.8 Minimum Detectable Limit (MDL).

$$\text{MDL} = 2.5 A[\text{si}] m[i] * / A[\text{ci}] * \text{RRF}[i]$$

Eq. 23-7

## 9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$n C[\text{Tr}] = \text{Sigma } C[i] \text{ } i = 1$$

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.
4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.
5. U.S. Environmental Protection Agency. Method 8290 -- The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW-846.

TABLE 1 -- COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS



Analyte	Concentration (pg/ mu l)
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/mu l)				
	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
Recovery Standards:					
<13> C [12] -1,2,3,4-TCDD	100	100	100	100	100
<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 [7] F [11]	PFK
	303.9016	M	C [12] H [4] <35> Cl [4] O	TCDF
	305.8987	M + 2	C [12] H [4] <35> Cl <37> O	TCDF
	315.9419	M	<13> C [12] H [4] <35> Cl [4] O	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[4]O[2]	TCDD (S)
	330.9792	QC	C[7]F[13]	PFK
	331.9368	M	<13>C[12]H[4]<35>Cl[4]O[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[2]O	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[2]O	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[2]O[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[2]O[2] (S)	PeCDD (S)
	375.8364	M + 2	C[12]H[4]<35>Cl[5]<37>ClO	HxCDFE
	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[2]O	HxCDF
	383.8639	M	<13>C[12]H[2]<35>Cl[6]O	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[2]O[2]	HxCDD
	392.9760	LOCK	C[9]F[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[2]O	HxCDD (S)
	455.7555	M + 4	C[12]H[2]<35>Cl[6]<37>Cl[2]O	OCDPE

430.9729 QC	C[9]F[17]	PFK
4 407.7818 M + 2	C[12]H<35>CI[6]<37>CIO	HpCDF
409.7789 M + 4	C[12]H<35>CI[5]<37>CI[2]O	HpCDF
417.8253 M	<13>C[12]H<35>CI[7]O	HpCDF (S)
419.8220 M + 2	<13>C[12]H<35>CI[6]<37>CIO	HpCDF (S)
423.7766 M + 2	C[12]H<35>CI[6]<37>CIO[2]	HpCDD
425.7737 M + 4	C[12]H<35>CI[5]<37>CI[2]O[2]	HpCDD
435.8169 M + 2	<13>C[12]H<35>CI[6]<37>CIO[2]	HpCDD (S)
437.8140 M + 4	<13>C[12]H<35>CI[5]<37>CI[2]O[2]	HpCDD (S)
479.7165 M + 4	C[12]H<35>CI[7]<<37>CI[2]O	NCPDE
430.9729 LOCK	C[9]F[17]	PFK
441.7428 M + 2	C[12]<35>CI[7]<37>CIO	OCDF
443.7399 M + 4	C[12]<35>CI[6]<37>CI[2]O	OCDF
457.7377 M + 2	C[12]<35>CI[7]<37>CIO[2]	OCDD
459.7348 M + 4	C[12]<35>CI[6]<37>CI[2]O[2]	OCDD
469.7779 M + 2	<13>C[12]<35>CI[7]<37>CIO[2]	OCDD (S)
471.7750 M + 4	<13>C[12]<35>CI[6]<37>CI[2]O[2]	OCDD (S)
513.6775 M + 4	C[12]<35>CI[8]<37>CI[2]O[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>CI = 34.968853

<37>CI = 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	of Ion type	Theo- retical 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

TABLE 4 -- ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S --  
Continued

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
6 4	M + 2 / M +	1.24	1.05	1.43

TABLE 4 -- ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S -- Continued

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
a 6	M/M + 2	0.51	0.43	0.59
b 7	M/M + 2	0.44	0.37	0.51
7 4	M + 2 / M +	1.04	0.88	1.20
8 4	M + 2 / M +	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	Daily calibration %
	RSD	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>CI[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. *Applicability and Principle*

1.1 **Applicability.** This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 **Principle.** Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

### 2. *Applicable Standard Methods*

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475-60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference -- see § 60.17).

2.2 ASTM D2369-81, Standard Test Method for Volatile Content of Coatings (incorporated by reference -- see § 60.17).

2.3 ASTM D3792-79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference -- see § 60.17).

2.4 ASTM D4017-81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference -- see § 60.17).

### 3. Procedure

3.1 Volatile Matter Content. Use the procedure in ASTM D2369-81 (incorporated by reference -- see § 60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W[1] = Weight of dish and sample before heating, g.

W[2] = Weight of dish and sample after heating, g.

W[3] = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in Section 4.3 is met. Calculate the weight fraction of the volatile matter (W[v]) for each analysis as follows:

$$W[v] = W[1] - W[2] / W[3]$$

Eq. 24-1

Record the arithmetic average (W[v]).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W[w]) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference -- see § 60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in Section 4.3 is met. Record the arithmetic average (W[w]).

3.3 Coating Density. Determine the density (D[c], kg/liter) of the surface coating using the procedure in ASTM D1475-60 (Reapproved 1980) (incorporated by reference -- see § 60.17).

Run duplicate sets of determinations for each coating until the criterion in Section 4.3 is met. Record the arithmetic average (D[c]).

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

### 4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by

running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

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

	<b>Within- laboratory</b>	<b>Between- laboratory</b>
Volatile matter content, W[v]	1.5 pct W[v]	4.7 pct W[v]
Water content, W[w]	2.9 pct W[w]	7.5 pct W[w.]
Density, D[c]	0.001 kg/liter	0.002 kg/liter.

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

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

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate between-laboratory precision value to the measured mean value for that parameter. For W[v] and D[c], use the lower confidence limits, and for W[w], use the upper confidence limit. Because V[s] is calculated, there is no adjustment for the parameter.

## 5. Calculations

### 5.1 Nonaqueous Volatile Matter.

#### 5.1.1 Solvent-borne Coatings.

$$W[o] = W[v]$$

Eq. 24-2

Where:

W[o] = Weight fraction nonaqueous volatile matter, g/g.

#### 5.1.2 Waterborne Coatings.

$$W[o] = W[v] - W[w]$$

Eq. 24-3

5.2 Weight Fraction Solids.

$$W[s] = 1 - W[v]$$

Eq. 24-4

Where:  $W[s]$  = Weight solids, g/g.

## METHOD 24A -- DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PRINTING INKS AND RELATED COATINGS

### 1. *Applicability and Principle*

1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.

1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

### 2. *Procedure*

#### 2.1 Weight Fraction VOC.

##### 2.1.1 Apparatus.

2.1.1.1 Weighing Dishes. Aluminum foil, 58 mm in diameter by 18 mm high, with a flat bottom. There must be at least three weighing dishes per sample.

2.1.1.2 Disposable Syringe. 5 ml.

2.1.1.3 Analytical Balance. To measure to within 0.1 mg.

2.1.1.4 Oven. Vacuum oven capable of maintaining a temperature of 120 +/- 2 deg. C and an absolute pressure of 510 +/- 51 mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of 120 +/- 2 deg. C for 24 hours.

2.1.2 Analysis. Shake or mix the sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight ( $M[x1]$ ).

Using a 5-ml syringe without a needle remove a sample of the coating. Weigh the syringe and sample to the nearest 0.1 mg and record this weight ( $M[cY1]$ ). Transfer 1 to 3 g of the sample to the tared weighing dish. Reweigh the syringe and sample to the nearest 0.1 mg and record this weight ( $M[cY2]$ ). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of 510 +/- 51 mm Hg and a temperature of 120 +/- 2 deg. C for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of 120 +/- 2 deg. C for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the



weight (M[x2]). Repeat this procedure for a total of three determinations for each sample.

2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D 1475-60 (Reapproved 1980), (incorporated by reference -- see § 60.17).

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

### 3. Calculations

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content W[o] using the following equation:

$$W[o] = \frac{M[x1] + M[cY1] - M[cY2] - M[x2]}{M[cY1] - M[cY2]}$$

Eq. 24A-1

Report the weight fraction VOC W[o] as the arithmetic average of the three determinations.

3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content V[o] using the following equation:

$$V[o] = \frac{W[o] D[c]}{D[o]}$$

Eq. 24A-2

### 4. Bibliography

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

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

### 1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and, therefore, a particulate filter is required. The minimum detectable for the method is 50 ppm as carbon.

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<sub>2</sub> and 10 percent water vapor, but it would be significant for a source near the detection limit having 10 percent CO<sub>2</sub> and 20 percent water vapor.

This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated 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.

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<sub>4</sub>) will, of course, also be measured. The FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions 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).

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

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

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a 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 CO<sub>2</sub> and quantitatively collecting the effluent in an evacuated vessel; then a portion of the CO<sub>2</sub> is reduced to CH<sub>4</sub> 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<sub>2</sub> and CH<sub>4</sub>; the NMO are oxidized to CO<sub>2</sub>, reduced to CH<sub>4</sub>, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

## 2. Apparatus

2.1 Sampling. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (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:

2.1.1 Heated Probe. 6.4-mm (1/4-in.) OD stainless steel tubing with a heating system capable of maintaining a gas temperature at the exit end of at least 129 deg. C (265 deg. F). The probe shall be equipped with a thermocouple 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 thermocouple 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.

2.1.2 Filter Holder. 25-mm (15/16-in.) ID Gelman filter holder with stainless steel body and stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

2.1.3 Filter Heating System. 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 deg. C (250 +/- 5 deg. F).

A suitable heating box is shown in Figure 25-2. The outer shell is a metal box that measures 102 mm X 280 mm X 292 mm (4 in. X 11 in. X 11 1/2 in.), while the inner shell is a metal box measuring 76 mm X 229 mm X 241 mm (3 in. X 9 in. X 9 1/2 in.). The inner box is supported by 13-mm (1/2-in.) phenolic rods. The void space between the boxes is filled with fiberfrax 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 temperature of 121 deg. C as measured by a thermocouple in the gas line just before the filter. An additional thermocouple is used to monitor the temperature of the gas behind the filter.

2.1.4 Condensate Trap. 9.5-mm (3/8-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/cc 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.

2.1.5 Valve. Stainless steel shut-off valve for starting and stopping sample flow.

2.1.6 Metering Valve. Stainless steel control valve for regulating the sample flow rate through the sample train.

2.1.7 Rotameter. Glass tube with stainless steel fittings, capable of measuring sample flow in the range of 60 to 100 cc/min.

2.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters.

2.1.9 Mercury Manometer or Absolute Pressure Gauge. Capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

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

2.2. Condensate Recovery Apparatus. The system for the recovery of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, 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 5.1. The following major components are required:

2.2.1. Heat Source. Sufficient to heat the condensate trap (including connecting tubing) to a temperature of 200 deg. C. A system using both a heat gun and an electric tube furnace is recommended.

2.2.2. Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 deg. C.

2.2.3. 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 (1/8-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. The catalyst tube shall be mounted vertically in a 650 deg. C tube furnace.

2.2.4 Water Trap. Leak proof, capable of removing moisture from the gas stream.

2.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

2.2.6 NDIR Detector. Capable of indicating CO<sub>2</sub> concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

2.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

2.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters are recommended.

2.2.9 Mercury Manometer or Absolute Pressure Gauge. Capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

2.2.10 Syringe. 10-ml gas-tight, glass syringe equipped with an appropriate needle.

2.3 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<sub>2</sub>, and CH<sub>4</sub> from NMO, (2) reducing the CO<sub>2</sub> to CH<sub>4</sub> and quantifying as CH<sub>4</sub>, and (3) oxidizing the NMO to CO<sub>2</sub>, reducing the CO<sub>2</sub> to CH<sub>4</sub> and quantifying as CH<sub>4</sub>, according to Section 5.2. The analyzer consists of the following major components:

2.3.1 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 deg. C furnace.

2.3.2 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 deg. C furnace.

2.3.3 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 deg. C with carrier gas flowing through them for 24 hours before initial use.

2.3.4 Sample Injection System. A 10-port GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

2.3.5 FID. An FID meeting the following specifications is required:

2.3.5.1 Linearity. A linear response (+/- 5 percent) over the operating range as demonstrated by the procedures

established in Section 5.2.3.

2.3.5.2 Range. A full scale range of 10 to 50,000 ppm CH<sub>4</sub>. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

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

2.4 Other Analysis Apparatus.

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

2.4.2 Thermometer. Capable of measuring the laboratory temperature to within 1 deg. C.

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

2.4.4 Syringes. 10-  $\mu$ l and 50-  $\mu$ l liquid injection syringes.

2.4.5 Liquid Sample Injection Unit. 316 SS U-tube fitted with an injection septum, see Figure 25-7.

### 3. Reagents

3.1 Sampling. The following are required for sampling:

3.1.1 Crushed Dry Ice.

3.1.2 Coarse Quartz Wool. 8 to 15  $\mu$ m.

3.1.3 Filters. Glass fiber filters, without organic binder.

3.2 NMO Analysis. The following gases are needed:

3.2.1 Carrier Gases. Zero grade helium (He) and oxygen (O<sub>2</sub>) containing less than 1 ppm CO<sub>2</sub> and less than 0.1 ppm C as hydrocarbon.

3.2.2 Fuel Gas. Zero grade hydrogen (H<sub>2</sub>), 99.999 percent pure.

3.2.3 Combustion Gas. Zero grade air or O<sub>2</sub> as required by the detector.

3.3 Condensate Analysis. The following gases are needed:

3.3.1 Carrier Gas. Zero grade air, containing less than 1 ppm C.

3.3.2 Auxiliary O<sub>2</sub>. Zero grade O<sub>2</sub>, containing less than 1 ppm C.

3.3.3 Hexane. ACS grade, for liquid injection.

3.3.4 Decane. ACS grade, for liquid injection.

3.4 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:

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

3.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.4.3 CO<sub>2</sub> Calibration Gases. Three gas mixture standards with nominal CO<sub>2</sub> concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

3.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

3.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH<sub>4</sub>, 2 percent CO<sub>2</sub>, and 20 ppm C<sub>3</sub>H<sub>8</sub>, prepared in air.

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

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

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

## 4. Procedure

### 4.1 Sampling.

4.1.1 Cleaning Sampling Equipment. Before its initial use and after each subsequent 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 the final paragraph of Section 4.3.3. A trap may be considered clean when the CO<sub>2</sub> concentration in its effluent gas drops below 10 ppm. This check is optional for traps that have been used to collect samples which were then recovered according to the procedure in Section 4.3.3.

4.1.2 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 no change in tank vacuum is noted. The evacuation and leak check may be conducted either in the laboratory or the field. The results of the leak check should be included in the test report.

4.1.3 Sample Train Assembly. Just before assembly, measure the tank vacuum using a mercury U-tube manometer or absolute pressure gauge. 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. The point where the inlet tube joins the trap body should be 2.5 to 5 cm above the top of the dry ice.

4.1.4 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 5 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 6.2. If the measured pressure change exceeds the calculated limit, correct the problem before beginning sampling. The results of the leak check should be included in the test report.

4.1.5 Sample Train Operation. 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 deg. C (265 deg. F) and the filter temperature controller to 121 deg. C (250 deg. F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cc/min, and purge the train with stack gas for at least 10 minutes. When the temperatures at the exit ends of the probe and filter are within their specified range, sampling may begin.

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 regulation; 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.

4.2 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 flowmetering system, 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. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that the test run number is properly identified on the condensate trap and the sample tank(s).

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

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

4.3.1.1 Leak Check. With the carrier gas inlets and the flow control valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Close the vacuum pump valve and turn off the vacuum pump. Monitor the system pressure for 10 minutes. The system is acceptable if the pressure change is less than 2 mm Hg.

4.3.1.2 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<sub>2</sub> content. The system background is acceptable if the CO<sub>2</sub> concentration is less than 10 ppm.

4.3.1.3 Oxidation Catalyst Efficiency Check. Conduct a catalyst efficiency test as specified in Section 5.1.2 of this method. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap CO<sub>2</sub> Purge and Sample Tank Pressurization. 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<sub>2</sub> 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.

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<sub>2</sub> 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.

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<sub>2</sub> concentration of the trap effluent is less than 5 ppm. CO<sub>2</sub> 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.

After the completion of the CO<sub>2</sub> purge, use the carrier gas bypass valve to pressurize the sample tank to approximately 1060 mm Hg absolute pressure with zero air.

4.3.3 Recovery of the Condensate Trap Sample. See Figure 25-10. 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.

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.

Now, 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<sub>2</sub> 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 deg. C. 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<sub>2</sub> 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<sub>2</sub> 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 deg. C. 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<sub>2</sub> concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO<sub>2</sub> purge Procedure, Section 4.3.2.

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.

**4.4 Analysis.** Before putting the NMO 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; then conduct the performance test according to the procedures established in Section 5.2. Once the performance test has been successfully completed and the CO<sub>2</sub> and NMO calibration response factors have been determined, proceed with sample analysis as follows:

**4.4.1 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 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (Section 5.2) before proceeding.

**4.4.2 Operating Conditions.** The carrier gas flow rate is 29.5 cc/min He and 2.2 cc/min O<sub>2</sub>. The column oven is heated to 85 deg. C. The order of elution for the sample from the column is CO, CH<sub>4</sub>, CO<sub>2</sub>, and NMO.

**4.4.3 Analysis of Recovered Condensate Sample.** Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO<sub>2</sub> in the sample will elute in approximately 100 seconds. As soon as the detector response returns to baseline following the CO<sub>2</sub> peak, switch the carrier gas flow to backflush, and raise the column oven temperature to 195 deg. C as rapidly as possible. A rate of 30 deg. C/min has been shown to be adequate. Record the value obtained for the condensible organic material (C<sub>cm</sub>) measured as CO<sub>2</sub> and any measured NMO. Return the column oven temperature to 85 deg. C in preparation for the next analysis. Analyze each sample in triplicate, and report the average C<sub>cm</sub>.

**4.4.4 Analysis of Sample Tank.** Perform the analysis as described in Section 4.4.3, but record only the value measured for NMO (C<sub>tm</sub>).

**4.5 Audit Samples.** Analyze a set of two audit samples concurrently with any compliance samples and in exactly the same manner to evaluate the analyst's technique and the instrument calibration. The same analysts, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples;

if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

Calculate the concentrations of the audit samples in ppm using the specified sample volume in the audit instructions. (NOTE. -- Indication of acceptable results may be obtained immediately by reporting the audit results in ppm and compliance results in ppm by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency during the 30-day period.

The concentration of the audit samples obtained by the analyst shall agree within 20 percent of the actual concentrations. Failure to meet the 20-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance of the affected facility.

### *5. Calibration and Operational Checks*

Maintain a record of performance of each item.

5.1 Initial Performance Check of 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 specified frequency.

5.1.1 Carrier Gas and Auxiliary O<sub>2</sub> Blank Check. Analyze each new tank of carrier gas or auxiliary O<sub>2</sub> with the NMO analyzer to check for contamination. Treat the gas cylinders as noncondensable gas samples, and analyze according to the procedure in Section 4.4.3. Add together any measured CH<sub>4</sub>, CO, CO<sub>2</sub>, or NMO. The total concentration must be less than 5 ppm.

5.1.2 Catalyst Efficiency Check. With a clean condensate trap installed in the recovery system, replace the carrier gas cylinder with the high level methane standard gas cylinder (Section 3.4.1). 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.

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 so that atmospheric pressure is maintained in the system within 10 percent. 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<sub>2</sub> using the NMO analyzer; the catalyst efficiency is acceptable if the CO<sub>2</sub> concentration is within 2 percent of the methane standard concentration.

5.1.3 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<sub>2</sub> 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 5.1.3.1 to 5.1.3.4) into the injection port. Operate the

trap recovery system as described in Section 4.3.3. Measure the final ICV pressure, and then analyze the vessel to determine the CO<sub>2</sub> concentration. For each injection, calculate the percent recovery using the equation in Section 6.6.

The performance test is acceptable if the average percent recovery is 100 +/- 10 percent with a relative standard deviation (Section 6.9) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 50 µl Hexane.

5.1.3.2 10 µl Hexane.

5.1.3.3 50 µl Decane.

5.1.3.4 10 µl Decane.

5.2 Initial NMO Analyzer Performance Test. 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.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (Section 3.4.1). The oxidation catalyst operation is acceptable if the FID response is less than 1 percent of the injected methane concentration.

5.2.2 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 3.4.1). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the response under both conditions agree within 5 percent.

5.2.3 Analyzer Linearity Check and NMO Calibration. While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in Section 3.4.2. Make triplicate injections of each calibration gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (Section 6.9) for each set of triplicate injections is less than 2 percent. 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<sub>2</sub> standards specified in Section 3.4.3. 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<sub>2</sub> calibration response factor (RF[CO<sub>2</sub>]). 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 for each set of triplicate injections is less than 2 percent. The RF[CO<sub>2</sub>] must be within 10 percent of the RF[NMO].

5.2.4 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in Section 3.4.4. 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.

5.3 NMO Analyzer Daily Calibration.

5.3.1 CO<sub>2</sub> Response Factor. Inject triplicate samples of the high level CO<sub>2</sub> calibration gas (Section 3.4.3), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF[CO<sub>2</sub>] calculated during the initial performance test (Section 5.2.3). Use the daily

response factor (DRF[CO<sub>2</sub>]) for analyzer calibration and the calculation of measured CO<sub>2</sub> concentrations in the ICV samples.

5.3.2 NMO Response Factors. Inject triplicate samples of the mixed propane calibration cylinder (Section 3.4.4.1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 5 percent of the RF[NMO] calculated during the initial performance test (Section 5.2.4). Use the daily response factor (DRF[NMO]) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 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.

## 6. 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.

### 6.1 Nomenclature.

C = TGNMO concentration of the effluent, ppm C equivalent.

C[c] = Calculated condensable organic (condensate trap) concentration of the effluent, ppm C equivalent.

C[cm] = Measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO<sub>2</sub>.

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

C[tm] = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.

F = Sampling flow rate, cc/min.

L = Volume of liquid injected, ml.

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

m[c] = TGNMO mass concentration of the effluent, mg C/dsm<sup>3</sup>.

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

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.

T[f] = Final temperature of intermediate collection vessel, deg. K.

$T[ti]$  = Sample tank temperature before sampling, deg. K.

$T[t]$  = Sample tank temperature at completion of sampling, deg. K.

$T[tf]$  = Sample tank temperature after pressurizing, deg. K.

$V$  = Sample tank volume, m<sup>3</sup>.

$V[t]$  = Sample train volume, cc.

$V[v]$  = Intermediate collection vessel volume, m<sup>3</sup>.

$V[s]$  = Gas volume sampled, dsm<sup>3</sup>.

$n$  = Number of data points.

$q$  = Total number of analyzer injections of intermediate collection vessel during analysis (where  $k$  = injection number, 1 . . .  $q$ ).

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

$x[i]$  = Individual measurements.

$\bar{x}$  = Mean value.

$\rho$  = Density of liquid injected, g/cc.

THETA = Leak check period, min.

DELTA P = Allowable pressure change, cm Hg.

6.2 Allowable Pressure Change. For the pretest leak check, calculate the allowable pressure change:

$$\text{DELTA P} = 0.01 \text{ FP}[b] \text{ THETA} / V[t]$$

Eq. 25-1

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

$$V[S] = 0.3857 V [P[t] / T[t] - P[ti] / T[ti]]$$

Eq. 25-2

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

$$C[t] = [P[tf] / T[tf] / P[t] / T[ti] - / T[t] T[ti] X 1/r \langle r \rangle \text{ SIGMA } [j = 1] C[tm][j]$$

Eq. 25-3

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

$$C[c] = 0.3857 V[v] P[f] / V[s] T[f] X [1 / q <q> SIGMA [k = 1] C[cm][k]$$

Eq. 25-4

6.6 TGNMO. To determine the TGNMO concentration for each test run, use the following equation:

$$C = C[t] + C[c]$$

Eq. 25-5

6.7 TGNMO Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$m[c] = 0.4993 C$$

Eq. 25-6

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

$$\text{Percent recovery} = 1.604 M / L X V[v] / P X P[t] / T[f] X C[cm] / N$$

Eq. 25-7

6.9 Relative Standard Deviation.

$$RSD = 100 / - x \text{ root} / SIGMA (x[1] - x)^2 / n - 1$$

Eq. 25-8

## 7. Bibliography

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.

Figure 25-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

Figure 25-2. Out-of-stack filter box.

[SEE FIGURE IN ORIGINAL]

Figure 25-3. Condensate trap.

[SEE FIGURE IN ORIGINAL]

Figure 25-4. Condensate recovery system.

[SEE FIGURE IN ORIGINAL]

Figure 25-5. Simplified schematic of nonmethane organic (NMO) analyzer.

[SEE FIGURE IN ORIGINAL]

Figure 25-6. Nonmethane organic analyzer (NMO).

[SEE FIGURE IN ORIGINAL]

Figure 25-7. Liquid sample injection unit.

[SEE FIGURE IN ORIGINAL]

Figure 25-8. Example field data form.

[SEE FIGURE IN ORIGINAL]

Figure 25-9. Condensate recovery system, CO<sub>2</sub> purge.

[SEE FIGURE IN ORIGINAL]

Figure 25-10. Condensate recovery system, collection of trap organics.

[SEE FIGURE IN ORIGINAL]

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

### *1. Applicability and Principle*

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

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

### *2. Definitions*

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

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

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

2.2 Span Value. The upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

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

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

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

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

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

### 3. Apparatus

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

Figure 26A 1. Organic Concentration Measurement System.

[SEE FIGURE IN ORIGINAL]

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

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

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

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

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



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

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

#### 4. *Calibration and Other Gases*

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

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

4.1 Fuel. A 40 percent H<sub>2</sub>/60 percent He or 40 percent H<sub>2</sub>/60 percent N<sub>2</sub> gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

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

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

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

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

#### 5. *Measurement System Performance Specifications*

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

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

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

#### 6. *Pretest Preparations*

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

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe,

or duct and is sealed tightly at the stack port connection.

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

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics (> 1.0 percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

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

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

## 7. Emission Measurement Test Procedure

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

## 8. Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C[c] = K C[\text{meas}]$$

Eq. 25A-1

Where:

$C[c]$  = Organic concentration as carbon, ppmv.

$C[\text{meas}]$  = Organic concentration as measured, ppmv.

$K$  = Carbon equivalent correction factor,

$K = 2$  for ethane.

$K = 3$  for propane.

$K = 4$  for butane.

$K$  = Appropriate response factor for other organic calibration gases.

## 9. *Bibliography*

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. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, NC. June 1978.
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.

## METHOD 25B -- DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

### 1. *Applicability and Principle*

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes. (Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.) The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

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

### 2. *Definitions*

The terms and definitions are the same as for Method 25A.

### 3. *Apparatus*

The apparatus is the same as for Method 25A with the exception of the following:

3.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

### 4. *Calibration Gases*

The calibration gases are the same as required for Method 25A, Section 4. No fuel gas is required for an NDIR.

### 5. *Measurement System Performance Specifications*

5.1 Zero Drift. Less than +/- 3 percent of the span value.

5.2 Calibration Drift. Less than +/- 3 percent of the span value.

5.3 Calibration Error. Less than +/- 5 percent of the calibration gas value.

### 6. *Pretest Preparations*

6.1 Selection of Sampling Site. Same as in Method 25A, Section 6.1.

6.2 Location of Sample Probe. Same as in Method 25A, Section 6.2.

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

6.4 Calibration Error Test. Same as in Method 25A, Section 6.4.

6.5 Response Time Test Procedure. Same as in Method 25A, Section 6.5.

### 7. *Emission Measurement Test Procedure*

Proceed with the emission measurement immediately upon satisfactory completion of the calibration.

7.1 Organic Measurement. Same as in Method 25A, Section 7.1.

7.2 Drift Determination. Same as in Method 25A, Section 7.2.

### 8. *Organic Concentration Calculations*

The calculations are the same as in Method 25A, Section 8.

### 9. *Bibliography*

The bibliography is the same as in Method 25A.

## 1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. This method is applicable for determining hydrogen chloride (HCl) emissions from stationary sources.

1.2 Principle. An integrated sample is extracted from the stack and passed through dilute sulfuric acid. In the dilute acid, the HCl gas is dissolved and forms chloride ( $\text{Cl}^-$ ) ions. The  $\text{Cl}^-$  is analyzed by ion chromatography (IC).

1.3 Interferences. Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences. Another likely interferent is diatomic chlorine ( $\text{Cl}_2$ ) gas which reacts to form HCl and hypochlorous acid (HOCl) upon dissolving in water. However,  $\text{Cl}_2$  gas exhibits a low solubility in water and the use of acidic, rather than neutral or basic collection solutions, greatly reduces the chance of dissolving any chlorine present. This method does not experience a significant bias when sampling a 400 ppm HCl gas stream containing 50 ppm  $\text{Cl}_2$ . Sampling a 220 ppm HCl gas stream containing 180 ppm  $\text{Cl}_2$  results in a positive bias of 3.4 percent in the HCl measurement.

1.4 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  $\text{Cl}_2$  when sampling at concentrations less than 50 ppm.

1.5 Stability. The collected samples can be stored for up to 4 weeks before analysis.

1.6 Detection Limit. The analytical detection limit of the method is 0.1  $\mu\text{g}/\text{ml}$ .

## 2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 26-1, and component parts are discussed below.

2.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system to prevent moisture condensation. A 3/8-in I.D. Teflon elbow should be attached to the inlet of the probe and a 1-in. (25-mm) length of 3/8-in. I.D. Teflon tubing should be attached to the open end of the elbow to permit the opening of the probe to be turned away from the gas stream. This reduces the amount of particulate entering the train. This probe configuration should be used when the concentration of particulate matter in the emissions is high. When high concentrations are not present, the Teflon elbow is not necessary, and the probe inlet may be perpendicular to the gas stream. A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result. Instead, a Teflon filter (see Section 2.1.5) should be installed at the inlet (for stack temperatures < 300 deg. F) or outlet (for stack temperatures > 300 deg. F) of the probe.

2.1.2 Three-way Stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect directly to the outlet of the probe 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.

Figure 26-1. Sampling train.

[SEE FIGURE IN ORIGINAL]

2.1.3 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 1 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.

2.1.4 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 deg. C (350 deg. F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

2.1.5 Filter. A 25-mm Teflon mat, Pallflex TX40H175 or equivalent. Locate between the probe liner and Teflon elbow in a glass or quartz filter holder in a filter box heated to 250 deg. F.

2.1.6 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

2.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min.

2.1.8 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.

2.1.9 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, Sections 2.1.4, 2.1.7, 2.1.8, 2.1.10, 2.1.11, and 2.1.12.

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

2.2.2 Storage Bottles. 100-ml glass, with Teflon-lined lids, to store impinger samples (two per sampling run). During clean-up, the two front impinger contents (0.1 N H<sub>2</sub>SO<sub>4</sub>) should be combined. The contents of the two rear impinger (0.1 N NaOH) may be discarded, as these solutions are included only to absorb Cl<sub>2</sub>, and thus protect the pump.

2.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

2.3.1 Volumetric Flasks. Class A, 100-ml size.

2.3.2 Volumetric Pipets. Class A, assortment. To dilute samples into the calibration range of the instrument.

2.3.3 Ion Chromatograph. Suppressed or nonsuppressed, 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 provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

### 3. Reagents

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.

3.1. Sampling.

3.1.1 Water. Deionized, distilled water that conforms to ASTM Specification D 1193-77, Type 3.

3.1.2 Absorbing solution, 0.1 N Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H<sub>2</sub>SO<sub>4</sub> 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.

3.1.3 Chlorine Scrubber Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the back pair of impingers, 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.

### 3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Blank Solution. A separate blank solution of the absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of absorbing solution to 100 ml with water in a separate volumetric flask.

3.2.3 Sodium Chloride (NaCl) Stock Standard Solution. Solutions containing a nominal certified concentration of 1000 mg/l are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl. The NaCl should be dried at 100 deg. C for 2 or more hours and 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. The exact Cl concentration can be calculated using Eq. 26-1.

$$\mu\text{g Cl}^-/\text{ml} = \text{g of NaCl} \times 10^3 \times 35.453 / 58.44$$

Eq. 26-1

Refrigerate the stock standard solution and store no longer than 1 month.

3.2.4 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.

## 4. Procedure

### 4.1 Sampling.

4.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the absorbing solution into each of the first two impingers, and add 15 ml of scrubber solution to the third and fourth impingers. Connect the impingers in series with the knockout impinger first, followed by the two impingers containing absorbing solution and the two containing the scrubber solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or Mae West impinger.

4.1.2 Leak-Check Procedures. Leak-check the probe and three-way stopcock before inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the probe and stopcock heating system to a temperature

sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak-check as described above. If a leak has occurred, the sampling run must be voided. Alternately, the portion of the train behind the probe may be leak-checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure 1A of Figure 26-1), and turn on the sampling pump. Pull a vacuum of at least 250 mm Hg, turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure 1B of Figure 26-2). If this procedure is used, the full train leak-check described above must be conducted following the final run, and all preceding sampling runs must be voided if a leak has occurred.

4.1.3 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. Purge for at least 5 minutes before sampling.

4.1.4 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 26-3). 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 5 minutes during the run. A sampling time of 1 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 4.1.2.

4.2 Sample Recovery. Disconnect the impingers after sampling. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two absorbing solution impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the scrubber impingers and connecting glassware rinses may be discarded. The sample bottle should be sealed, shaken to mix, and labeled. 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.

4.3 Sample Preparation for Analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. Quantitatively transfer the sample solution to a 100-ml volumetric flask, and dilute the solution to 100 ml with water.

4.4 Sample Analysis.

4.4.1 The IC conditions will depend upon analytical column type and whether suppressed or nonsuppressed IC is used. An example chromatogram from a nonsuppressed system using a 150-mm Hamilton PRP-X100 anion column, a \* \* \*. 2 l/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50  $\mu$ l sample loop, and a conductivity detector set on 1.0  $\mu$ S full scale is shown in Figure 26-2.

4.4.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl $\leftrightarrow$  appears in the chromatogram. If Cl $\leftrightarrow$  is present, repeat the load/injection procedure until no Cl $\leftrightarrow$  is present. At this point, the instrument is ready for use.

4.4.3 First, inject the calibration standards covering an appropriate concentration range, starting with the lowest concentration standard. Next, inject in duplicate, a QC sample followed by a water blank and the field samples. Finally, repeat the injection of calibration standards to allow compensation for any drift in the instrument during analysis of the field samples. Measure the Cl $\leftrightarrow$  peak areas or heights of the samples. Use the average response



from the duplicate injections to determine the field sample concentrations using a linear calibration curve generated from the standards.

4.5 Audit Analysis. An audit sample must be analyzed, subject to availability.

Figure 26-2. Example Chromatogram

[SEE FIGURE IN ORIGINAL]

## 5. Calibration

5.1 Dry Gas Metering System, Thermometers, Rate Meter, and Barometer. Same as in Method 6, sections 5.1, 5.2, 5.3, and 5.4.

5.2 Calibration Curve for Ion Chromatograph. To prepare calibration standards, dilute given volumes (1.0 ml or greater) of the stock standard solution, with 0.1 N H<sub>2</sub>SO<sub>4</sub> (section 3.1.2) to convenient volumes. Prepare at least four standards that are within the linear range of the instrument and which cover the expected concentration range of the field samples. Analyze the standards as instructed in section 4.4.3, beginning with the lowest concentration standard. Determine the peak measurements, and plot individual values versus Cl<sup>-</sup> concentration in  $\mu\text{g/ml}$ . Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

## 6. Quality Assurance

6.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of two audit samples must be analyzed.

6.2 Audit Procedure. The audit sample are chloride solutions. Concurrently analyze the two audit samples and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples. If this condition is met, auditing the subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

6.3 Audit Sample Availability. The audit samples may be obtained by writing or calling the EPA Regional Office or the appropriate enforcement agency. The request for the audit samples must be made at least 30 days prior to the scheduled compliance sample analyses.

6.4 Audit Results. Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions.

NOTE: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total  $\mu\text{g HCl/sample}$  to the responsible enforcement agency. Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA Regional Office or the appropriate enforcement agency. Include this information with subsequent analyses for the same enforcement agency during the 30-day period.

The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report.

Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

## 7. Calculations

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.

7.1 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6-1 of Method 6.

7.2 Total  $\mu\text{g}$  HCl Per Sample.

$$m = (S - B) \times (100) \times (36.46) / (35.453) = (102.84) \times (S - B)$$

Eq. 26-2

where:

$m$  = Mass of HCl in sample,  $\mu\text{g}$ .

$S$  = Concentration of sample,  $\mu\text{g Cl}^-/\text{ml}$ .

$B$  = Concentration of blank,  $\mu\text{g Cl}^-/\text{ml}$ .

100 = Volume of filtered and diluted sample, ml.

36.46 = Molecular weight of HCl,  $\mu\text{g} / \mu\text{g-mole}$ .

35.453 = Atomic weight of Cl,  $\mu\text{g} / \mu\text{g-mole}$ .

7.3 Concentration of HCl in the Flue Gas.

$$C = K[m] / V[m(\text{std})]$$

Eq. 26-3

where:

$C$  = Concentration of HCl, dry basis,  $\text{mg/dscm}$ .

$K = 10^{-3}$   $\text{mg}/\mu\text{g}$ .

$m$  = Mass of HCl in sample,  $\mu\text{g}$ .

$V[m(\text{std})]$  = Dry gas volume measured by the dry gas meter, corrected to standard conditions,  $\text{dscm}$ .

## 8. Bibliography

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2. State of California, Air Resources Board. Method 421. "Determination of Hydrochloric Acid Emissions from Stationary Sources." March 18, 1987.

3. Entropy Environmentalists Inc. "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report." EPA Contract No. 68-02-4442. Research Triangle Park, NC. January 22, 1988.

## METHOD 27--DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE DELIVERY TANK USING PRESSURE-VACUUM TEST

### 1. *Applicability and Principle*

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery tank which is equipped with vapor collection equipment.

1.2 Principle. Pressure and vacuum are applied alternately to the compartments of a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

### 2. *Definitions and Nomenclature*

2.1 Gasoline. Any petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

2.2 Delivery Tank. Any container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

2.3 Compartment. A liquid-tight division of a delivery tank.

2.4 Delivery Tank Vapor Collection Equipment. Any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

2.5 Time Period of the Pressure or Vacuum Test (t). The time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

2.6 Initial Pressure (P[i]). The pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.7 Initial Vacuum (V[i]). The vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.8 Allowable Pressure Change (DELTA p). The allowable amount of decrease in pressure during the static pressure test, within the time period t, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.9 Allowable Vacuum Change (DELTA v). The allowable amount of decrease in vacuum during the static vacuum test, within the time period t, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

### 3. Apparatus

3.1 Pressure Source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm H<sub>2</sub>O above atmospheric pressure.

3.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

3.3 Vacuum Source. Vacuum pump capable of evacuating the delivery tank to 250 mm H<sub>2</sub>O below atmospheric pressure.

3.4 Pressure-Vacuum Supply Hose.

3.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm H<sub>2</sub>O gauge pressure with +/- 2.5 mm H<sub>2</sub>O precision.

3.6 Pressure-Vacuum Relief Valves. The test apparatus shall be equipped with an in-line pressure-vacuum relief valve set to activate at 675 mm H<sub>2</sub>O above atmospheric pressure or 250 mm H<sub>2</sub>O below atmospheric pressure, with a capacity equal to the pressurizing or evacuating pumps.

3.7 Test Cap for Vapor Recovery Hose. This cap shall have a tap for manometer connection and a fitting with shut-off valve for connection to the pressure-vacuum supply hose.

3.8 Caps for Liquid Delivery Hoses.

### 4. Pretest Preparations

4.1 Summary. Testing problems may occur due to the presence of volatile vapors and/or temperature fluctuations inside the delivery tank. Under these conditions, it is often difficult to obtain a stable initial pressure at the beginning of a test, and erroneous test results may occur. To help prevent this, it is recommended that, prior to testing, volatile vapors be removed from the tank and the temperature inside the tank be allowed to stabilize. Because it is not always possible to attain completely these pretest conditions a provision to ensure reproducible results is included. The difference in results for two consecutive runs must meet the criterion in Sections 5.2.5 and 5.3.5.

4.2 Emptying of Tank. The delivery tank shall be emptied of all liquid.

4.3 Purging of Vapor. As much as possible, the delivery tank shall be purged of all volatile vapors by any safe, acceptable method. One method is to carry a load of non-volatile liquid fuel, such as diesel or heating oil, immediately prior to the test, thus flushing out all the volatile gasoline vapors. A second method is to remove the volatile vapors by blowing ambient air into each tank compartment for at least 20 minutes. This second method is usually not as effective and often causes stabilization problems, requiring a much longer time for stabilization problems, requiring a much longer time for stabilization during the testing.

4.4 Temperature Stabilization. As much as possible, the test shall be conducted under isothermal conditions. The temperature of the delivery tank should be allowed to equilibrate in the test environment. During the test, the tank should be protected from extreme environmental and temperature variability, such as direct sunlight.

### 5. Test Procedure

5.1 Preparations.

5.1.1 Open and close each dome cover.

5.1.2 Connect static electrical ground connections to tank. Attach the liquid delivery and vapor return hoses, remove the liquid delivery elbows, and plug the liquid delivery fittings.

5.1.3 Attach the test cap to the end of the vapor recovery hose.

5.1.4 Connect the pressure-vacuum supply hose and the pressure-vacuum relief valve to the shut-off valve. Attach a manometer to the pressure tap.

5.1.5 Connect compartments of the tank internally to each other if possible. If not possible, each compartment must be tested separately, as if it were an individual delivery tank.

## 5.2 Pressure Test.

5.2.1 Connect the pressure source to the pressure-vacuum supply hose.

5.2.2 Open the shut-off valve in the vapor recovery hose cap. Applying air pressure slowly, pressurize the tank to  $P[i]$ , the initial pressure specified in the regulation.

5.2.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain pressure of  $P[i]$ . When the pressure stabilizes, record the time and initial pressure.

5.2.4 At the end of  $t$  minutes, record the time and final pressure.

5.2.5 Repeat steps 5.2.2 through 5.2.4 until the change in pressure for two consecutive runs agrees within  $\pm 12.5$  mm H<sub>2</sub>O.

Calculate the arithmetic average of the two results.

5.2.6 Compare the average measured change in pressure to the allowable pressure change, DELTA  $p$ , as specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the pressure test until the criterion is met.

5.2.7 Disconnect the pressure source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

## 5.3 Vacuum Test.

5.3.1 Connect the vacuum source to the pressure-vacuum supply hose.

5.3.2 Open the shut-off valve in the vapor recovery hose cap. Slowly evacuate the tank to  $V[i]$ , the initial vacuum specified in the regulation.

5.3.3 Close the shut-off valve and allow the pressure in the tank to stabilize, adjusting the pressure if necessary to maintain a vacuum of  $V[i]$ . When the pressure stabilizes, record the time and initial vacuum.

5.3.4 At the end of  $t$  minutes, record the time and final vacuum.

5.3.5 Repeat steps 5.3.2 through 5.3.4 until the change in vacuum for two consecutive runs agrees within  $\pm 12.5$  mm H<sub>2</sub>O. Calculate the arithmetic average of the two results.

5.3.6 Compare the average measured change in vacuum to the allowable vacuum change, DELTA  $v$ , as

specified in the regulation. If the delivery tank does not satisfy the vapor tightness criterion specified in the regulation, repair the sources of leakage, and repeat the vacuum test until the criterion is met.

5.3.7 Disconnect the vacuum source from the pressure-vacuum supply hose, and slowly open the shut-off valve to bring the tank to atmospheric pressure.

5.4 Post-Test Clean-Up. Disconnect all test equipment and return the delivery tank to its pretest condition.

## 6. *Alternative Procedures*

6.1 The pumping of water into the bottom of a delivery tank is an acceptable alternative to the pressure source described above. Likewise, the draining of water out of the bottom of a delivery tank may be substituted for the vacuum source. Note that some of the specific step-by-step procedures in the method must be altered slightly to accommodate these different pressure and vacuum sources.

6.2 Techniques other than specified above may be used for purging and pressurizing a delivery tank, if prior approval is obtained from the Administrator. Such approval will be based upon demonstrated equivalency with the above method.

## METHOD 28 -- CERTIFICATION AND AUDITING OF WOOD HEATERS

### 1. *Applicability and Principle*

1.1 **Applicability.** This method is applicable for the certification and auditing of wood heaters. This method describes the test facility, test fuel charge, and wood heater operation as well as procedures for determining burn rates and particulate emission rates and for reducing data.

1.2 **Principle.** 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.

### 2. *Definitions*

2.1 **Burn Rate.** The rate at which test fuel is consumed in a wood heater. Measured in kilograms of wood (dry basis) per hour (kg/hr).

2.2 **Certification or Audit Test.** A series of at least four test runs conducted for certification or audit purposes that meets the burn rate specifications in Section 5.

2.3 **Firebox.** The chamber in the wood heater in which the test fuel charge is placed and combusted.

2.4 **Secondary Air Supply.** 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.

2.5 **Test Facility.** The area in which the wood heater is installed, operated, and sampled for emissions.

2.6 **Test Fuel Charge.** The collection of test fuel pieces placed in the wood heater at the start of the emission test run.

2.7 **Test Fuel Crib.** The arrangement of the test fuel charge with the proper spacing requirements between adjacent fuel pieces.

2.8 Test Fuel Loading Density. The weight of the as-fired test fuel charge per unit volume of usable firebox.

2.9 Test Fuel Piece. The 2 X 4 or 4 X 4 wood piece cut to the length required for the test fuel charge and used to construct the test fuel crib.

2.10 Test Run. An individual emission test which encompasses the time required to consume the mass of the test fuel charge.

2.11 Usable Firebox Volume. The volume of the firebox determined using the following definitions:

2.11.1 Height. 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.

2.11.2 Length. The longest horizontal fire chamber dimension that is parallel to a wall of the chamber.

2.11.3 Width. The shortest horizontal fire chamber dimension that is parallel to a wall of the chamber.

2.12 Wood Heater. An enclosed, woodburning appliance capable of and intended for space heating or domestic water heating, as defined in the applicable regulation.

2.13 Pellet Burning Wood Heater. 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. Apparatus*

3.1 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. Standard 103 (incorporated by reference. See § 60.17).

3.2 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.

3.3 Wood Heater Temperature Monitors. Seven, each capable of measuring temperature to within 1.5 percent of expected absolute temperatures.

3.4 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.

3.5 Balance (optional). Balance capable of weighing the test fuel charge to within 0.05 kg (0.1 lb).

3.6 Moisture Meter. Calibrated electrical resistance meter for measuring test fuel moisture to within 1 percent moisture content.

3.7 Anemometer. Device capable of detecting air velocities less than 0.10 m/sec (20 ft/min), for measuring air

velocities near the test appliance.

3.8 Barometer. Mercury, aneroid or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg).

3.9 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<sub>2</sub>O).

3.10 Humidity Gauge. Psychrometer or hygrometer for measuring room humidity.

3.11 Sampling Methods. Use particulate emission measurement Method 5G or Method 5H to determine particulate concentrations, gas flow rates, and particulate emission rates.

#### *4. Test Facility, Test Fuel Properties, and Test Fuel Charge Specifications*

##### 4.1 Test Facility.

4.1.1 Wood Heater Flue. 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.

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.

4.1.2 Test Facility Conditions. The test facility temperature shall be maintained between 18 and 32 degrees C (65 and 90 degrees F) during each test run.

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.

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<sub>2</sub>O) on the wood heater measured when the wood heater is not operating.

For test facilities with artificially induced barometric pressures (e.g., pressurized chambers), the barometric pressure in the test facility shall not exceed 1,033 mb (30.5 in. Hg) during any test run.

4.2 Test Fuel Properties. The test fuel shall conform to the following requirements:

4.2.1 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).

4.2.2 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.



4.2.3 Fuel Temperature. The test fuel shall be at the test facility temperature 18 to 32 degrees C (65 to 90 degrees F).

#### 4.3 Test Fuel Charge Specifications.

4.3.1 Fuel Dimensions. The dimensions of each test fuel piece shall conform to the nominal measurements of 2 X 4 and 4 X 4 lumber. Each piece of test fuel (not including spacers) shall be of equal length, except as necessary to meet requirements in Section 6.2.5, 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:

4.3.1.1 If the usable firebox volume is less than or equal to 0.043 m<sup>3</sup> (1.5 ft<sup>3</sup>), use 2 X 4 lumber.

4.3.1.2 If the usable firebox volume is greater than 0.043 m<sup>3</sup> (1.5 ft<sup>3</sup>) and less than or equal to 0.085 m<sup>3</sup> (3.0 ft<sup>3</sup>), use 2 X 4 and 4 X 4 lumber. About half the weight of the test fuel charge shall be 2 X 4 lumber, and the remainder shall be 4 X 4 lumber.

4.3.1.3 If the usable firebox volume is greater than 0.085 m<sup>3</sup> (3.0 ft<sup>3</sup>), use 4 X 4 lumber.

4.3.2 Test Fuel Spacers. Air-dried, Douglas fir lumber meeting the fuel properties in Section 4.2. The spacers shall be 130 X 40 X 20 mm (5 X 1.5 X 0.75 in.).

4.3.3 Test Fuel Charge Density. The test fuel charge density shall be 112 +/- 11.2 kg / m<sup>3</sup> (7 +/- 0.7 lb/ft<sup>3</sup>) of usable firebox volume on a wet basis.

4.4 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 degrees C (125 degrees F).

### 5. Burn Rate Criteria

5.1 Burn Rate Categories. One emission test run is required in each of the following burn rate categories:

#### BURN RATE CATEGORIES

(Average kg/hr, dry basis)

Category 1	Category 2	Category 3	Category 4
< 0.80	0.80 to 1.25	1.25 to 1.90	Maximum burn rate.

5.1.1 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.

5.1.2 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.

5.2 Alternative Burn Rates for Burn Rate Categories 1 and 2. If a wood heater cannot be operated at a burn rate below 0.80 kg/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, the flue shall be dampered or the air supply otherwise controlled in order to achieve two test runs within Category 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 6.4.3. Report the evidence and the reasoning used to determine that a test in burn rate Category 1 cannot be achieved; for example, two attempts to operate at a burn rate of 0.4 kg/hr are not sufficient evidence that burn rate Category 1 cannot be achieved.

## 6. Procedures

6.1 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.

6.1.1 Catalyst-equipped Wood Heater. Operate the catalyst-equipped wood heater using fuel described in Section 4.2 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 6.2.2) and the hours of operation.

6.1.2 Non-Catalyst Wood Heater. Operate the wood heater using the fuel described in Section 6.1.1 at a medium burn rate for at least 10 hours. Record and report the hours of operation.

6.2 Pretest Preparation. Record the test fuel charge dimensions and weights, and wood heater and catalyst descriptions as shown in the example in Figure 28-3.

6.2.1 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 4.1.1. Clean the flue with an appropriately sized, wire chimney brush before each certification test.

6.2.2 Wood Heater Temperature Monitors. 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.

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).

6.2.3 Test Facility Conditions. 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 degrees sector in front of the wood heater.

Use an anemometer to measure the air velocity. Measure and record the room air velocity before the pretest ignition period (Section 6.3) and once immediately following the test run completion.

Measure and record the test facility's ambient relative humidity, barometric pressure, and temperature before and after each test run.

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 6.4.2).

6.2.4 Wood Heater Firebox Volume. Determine the firebox volume using the definitions for height, width, and length in Section 2. 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.

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.

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).

6.2.5 Test Fuel Charge. Prepare the test fuel pieces in accordance with the specifications in Section 4.3. Determine the test fuel moisture content with a calibrated electrical resistance meter or other equivalent performance meter. (To convert moisture meter readings from the dry basis to the wet basis:  $(100)(\text{percent dry reading}) / (100 + \text{percent dry reading}) = \text{percent moisture wet basis}$ .) 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.

Attach the spacers to the test fuel pieces with uncoated, ungalvanized nails or staples as illustrated in Figure 28-1. Attachment of spacers to the top of the test fuel piece(s) on top of the test fuel charge is optional.

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.

6.2.6 Sampling Method. Prepare the sampling equipment as defined by the selected method. Collect one

particulate emission sample for each test run.

6.2.7 Secondary Air Adjustment Validation. If design drawings do not show the introductions of secondary air into a chamber outside the firebox (Section 2.4), conduct a separate test of the wood heater's secondary air supply. Operate the wood heater at a burn rate in Category 1 (Sections 5.1 or 5.2) with the secondary air supply operated following the manufacturer's written instructions. Start the secondary air validation test run as described in Section 6.4.1, except no emission sampling is necessary and burn rate data shall be recorded at 5-minute intervals.

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.

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 6.4. 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.

6.3 Pretest Ignition. Build a fire in the wood heater in accordance with the manufacturer's written instructions.

6.3.1 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 4.2. The pretest fuel charge shall consist of whole 2 x 4's that are no less than 1/3 the length of the test fuel pieces. Pieces of 4 x 4 lumber in approximately the same weight ratio as for the test fuel charge may be added to the pretest fuel charge.

6.3.2 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.

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.

6.4 Test Run. Complete a test run in each burn rate category, as follows:

6.4.1 Test Run Start. 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.

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<sup>3</sup> (1.5 and 3.0 ft<sup>3</sup>), alternate the piece sizes in vertical stacking layers to the extent possible. For example, place 2 x 4's on the bottom layer in direct contact with the coal bed and 4 x 4's on the next layer, etc. (See Figure 28-2). 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 6.2.5.

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.

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 6.4.3 and 6.4.4) 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.

6.4.2 Data Recording. Record 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 at 10-minute intervals (or more frequently at the option of the tester) as shown on example data sheet, Figure 28-4.

6.4.3 Test Fuel Charge Adjustment. The test fuel charge may be adjusted (i.e., re-positioned) 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 (0.11lb) or 1.0 percent, whichever is greater) weight change. The time used to make this adjustment shall be less than 15 seconds.

6.4.4 Air Supply Adjustment. Secondary air supply controls may be adjusted once during the test run following the manufacturer's written instructions (see Section 6.2.7). 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.

6.4.5 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 5 and 6 and report the results. As an alternative to repeating all test runs without the heat exchange blower operating, the tester may conduct one test run without the blower operating as described in Section 6.4.5 at a burn rate in Category 2 (Section 5.1). 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 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.

6.5 Consecutive Test Runs. Test runs on a wood heater may be conducted consecutively provided that a minimum one-hour interval occurs between test runs.

6.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the burn rate categories specified in Section 5.1. 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 8.1). 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 5.2).

6.7 Pellet Burning Heaters. Certification testing procedures for pellet burning wood heaters are based on the procedures in this method. The differences in the procedures from the sections in Method 28 are as follows:

6.7.1 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-D2016-74(82)(Method A) or ASTM D4442-84. (incorporated by reference. See Section 60.17).

6.7.2 Test Fuel Charge Specifications. The test fuel charge size shall be as per the manufacturer's written instructions for maintaining the desired burn rate.

6.7.3 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.

6.7.4 Heater Installation. Arrange the heater with the fuel supply hopper on the platform scale as described in Section 6.2.1.

6.7.5 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.

6.7.6 Sampling Method. Method 5G or 5H shall be used for the certification testing of pellet burners. Prepare the sampling equipment as described in Method 5G or 5H. Collect one particulate emission sample for each test run.

6.7.7 Test Run. Complete a test run in each burn rate category as follows:

6.7.7.1 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.

6.7.7.2 Data Recording. Record the fuel (wood heater) weight data, wood heater temperature and operational data, and emission sampling data as described in Section 6.4.2.

6.7.7.3 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.

6.7.8 Calculations. Determine the burn rate using the difference between the initial and final fuel (wood heater) weights and the procedures described in Section 8.3. Complete the other calculations as described in Section 8.

## 7. *Calibrations*

7.1 Platform Scale. Perform a multipoint 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 20 percent to 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 lbs) 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.

7.2 Balance (optional). Calibrate as described in Section 7.1.

7.3 Temperature Monitor. Calibrate as in Method 2, Section 4.3, before the first certification test and semiannually thereafter.

7.4 Moisture Meter. Calibrate as per the manufacturer's instructions before each certification test.

7.5 Anemometer. Calibrate the anemometer as specified by the manufacturer's instructions before the first certification test and semiannually thereafter.

7.6 Barometer. Calibrate against a mercury barometer before the first certification test and semiannually thereafter.

7.7 Draft Gauge. Calibrate as per the manufacturer's instructions; a liquid manometer does not require calibration.

7.8 Humidity Gauge. Calibrate as per the manufacturer's instructions before the first certification test and semiannually thereafter.

## 8. *Calculations and Reporting*

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

8.1 Weighted Average Emission Rate.

$$E[w] = \frac{\sum_{i=1}^n K[i] E[i]}{\sum_{i=1}^n K[i]}$$

Eq. 28-1

where:

$E[w]$  = Weighted average emission rate, g/hr;

$E[i]$  = Emission rate for test run,  $i$ , from Method 5G or 5H, g/hr;

$k[i]$  = Test run weighting factor =  $P[i+1] - P[i-1]$ ;

$n$  = Total number of test runs;

$P[1]$  = 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.

Note:  $P[0]$  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 shown on Figure 28-5.

8.2 Average Wood Heater Surface Temperatures. Calculate the average of the wood heater surface temperatures for the start of the test run (Section 6.3.1) and for the test run completion (Section 6.3.6). If the two average temperatures do not agree within 70 degrees C (125 degrees 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.

8.3 Burn Rate.

$BR = 60 W[wd] / \theta 100$  -- percent Mw / 100

Eq. 28-2

Where:

$BR$  = Dry wood burn rate, kg/hr (lb/hr)

$W[wd]$  = Total mass of wood burned during the test run, kg(lb)

$\theta$  -- Total time of test run, min.

$\%M[w]$  = Average moisture in test fuel charge, wet basis, percent.

8.4 Reporting Criteria. Submit both raw and reduced test data for wood heater tests. Specific reporting requirements are as follows:

8.4.1 Wood Heater Identification. Report wood heater identification information. An example data form is shown on Figure 28-4.

8.4.2 Test Facility Information. Report test facility temperature, air velocity, and humidity information. An example data form is shown on Figure 28-4.

8.4.3 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.

8.4.4 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.

8.4.5 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.

8.4.6 Suggested Test Report Format.

*a. Introduction*

1. Purpose of test -- certification, audit, efficiency, research and development.
2. Wood heater identification -- manufacturer, model number, catalytic/ noncatalytic options.
3. Laboratory -- name, location (altitude), participants.
4. Test information -- date wood heater received, date of tests, sampling methods used, number of test runs.

*b. Summary and Discussion of Results*

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).
2. Summary of other data -- test facility conditions, surface temperature averages, catalyst temperature averages, pretest fuel weights, test fuel charge weights, run times.
3. Discussion -- Burn rate categories achieved, test run result selection, specific test run problems and solutions.

*c. Process Description*

1. Wood heater dimensions -- volume, height, width, lengths (or other linear dimensions), weight, volume adjustments.
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).
3. Process operation during test -- air supply settings and adjustments, fuel bed adjustments, draft.
4. Test fuel -- test fuel properties (moisture and temperature), test fuel crib description (include line drawing or photograph), test fuel charge density.

*d. Sampling Locations*

Describe sampling location relative to wood heater. Include drawing or photograph.

*e. Sampling and Analytical Procedures*

1. Sampling methods -- brief reference to operational and sampling procedures and optional and alternative

procedures used.

2. Analytical methods -- brief description of sample recovery and analysis procedures.

*f. Quality Control and Assurance Procedures and Results*

1. Calibration procedures and results -- certification procedures, sampling and analysis procedures.

2. Test method quality control procedures -- leak-checks, volume meter checks, stratification (velocity) checks, proportionality results.

APPENDICES

1. Results and Example Calculations. Complete summary tables and accompanying examples of all calculations.

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.

3. Sampling and Analytical Procedures. Detailed description of procedures followed by laboratory personnel in conducting the certification test, emphasizing particularly parts of the procedures differing from the methods (e.g., approved alternatives).

4. Calibration Results. Summary of all calibrations, checks, and audits pertinent to certification test results with dates.

5. Participants. Test personnel, manufacturer representatives, and regulatory observers.

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).

7. Additional Information. Wood heater manufacturer's written instructions for operation during the certification test.

*9. Bibliography*

1. Oregon Department of Environmental Quality Standard Method for Measuring the Emissions and Efficiencies of Woodstoves, June 8, 1984. Pursuant to Oregon Administrative Rules Chapter 340, Division 21.

2. American Society for Testing Materials. Proposed Test Methods for Heating Performance and Emissions of Residential Wood-Fired Closed Combustion-Chamber Heating Appliances. E-6 Proposal P 180. August, 1986.

3. 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.

Figure 28-1. Test fuel spacer dimensions.

[SEE FIGURE IN ORIGINAL]

Figure 28-2. Test fuel crib arrangements

[SEE FIGURE IN ORIGINAL]

Figure 28-3. Wood Heater and Test Fuel Information.

[SEE FIGURE IN ORIGINAL]

Figure 28-4. Test run wood heater operation data sheet

[SEE FIGURE IN ORIGINAL]

FIGURE 28-5 -- EXAMPLE CALCULATION OF WEIGHTED AVERAGE EMISSION RATE

Burn rate category	Burn		
	Test number	rate Dry-kg/hr)	Emis-sions (g/hr)
1	1	0.65	5.0
2 n1	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

n1 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 number	Burn rate	P[1] P1	E[1] E1	K[1] K1
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

$$K[1] = P[2] - P[0] = RHO[0] = 0.300 - 0 = 0.300$$

$$K[2] = P[3] - P[1] = 0.380 - 0.121 = 0.259$$

$$K[3] = P[4] - P[2] = 0.722 - 0.300 = 0.422$$

$$K[4] = P[5] - P[3] = 0.912 - 0.380 = 0.532$$

$$K[5] = P[6] - P[4] = 1 - 0.722 = 0.278$$

$$n \langle n \rangle \text{SIGMA } [i = 1] \times K[i] = 0.300 + 0.259 + 0.422 + 0.532 + 0.278$$

$$\langle n \rangle \text{SIGMA } [i = 1] = 1.791 \quad E[w] = \langle n \rangle \text{SIGMA } [i = 1] \times (K[i]E[i]) / \langle n \rangle \text{SIGMA } [i = 1] \times K[i]$$

$$E[w] = (0.3)(5.0) + (0.259)(4.7) + (0.422)(5.3) + (0.532)(3.8) + (0.278)(5.1) \text{ divided by } 1.791$$

$$\text{EPSILON } [w] = 4.69 \text{ g/hr.}$$

TABLE 28-1 -- BURN RATE WEIGHTED PROBABILITIES FOR CALCULATING WEIGHTED AVERAGE EMISSION RATES

Burn rate (kg/hr-dry)	Cumulative Probability (P)
0.00	0.000
0.05	0.002
0.10	0.007
0.15	0.012
0.20	0.016
0.25	0.021
0.30	0.028
0.35	0.033
0.40	0.041
0.45	0.054
0.50	0.065
0.55	0.086
0.60	0.100
0.65	0.121
0.70	0.150
0.75	0.185
0.80	0.220
0.85	0.254
0.90	0.300
0.95	0.328
1.00	0.380
1.05	0.407
1.10	0.460
1.15	0.490
1.20	0.550
1.25	0.572
1.30	0.620
1.35	0.654
1.40	0.695
1.45	0.722
1.50	0.750
1.55	0.779
1.60	0.800
1.65	0.825

1.70	0.840
1.75	0.857
1.80	0.875
1.85	0.882
1.90	0.895
1.95	0.906
2.00	0.912
2.05	0.920
2.10	0.925
2.15	0.932
2.20	0.936
2.25	0.940
2.30	0.945
2.35	0.951
2.40	0.956
2.45	0.959
2.50	0.964
2.55	0.968
2.60	0.972
2.65	0.975
2.70	0.977
2.75	0.979
2.80	0.980
2.85	0.981
2.90	0.982
2.95	0.984
3.00	0.984
3.05	0.985
3.10	0.986
3.15	0.987
3.20	0.987
3.25	0.988
3.30	0.988
3.35	0.989
3.40	0.989
3.45	0.989
3.50	0.990
3.55	0.991
3.60	0.991
3.65	0.992
3.70	0.992
3.75	0.992
3.80	0.993
3.85	0.994
3.90	0.994
3.95	0.994
4.00	0.994
4.05	0.995
4.10	0.995
4.15	0.995

4.20	0.995
4.25	0.995
4.30	0.996
4.35	0.996
4.40	0.996
4.45	0.996
4.50	0.996
4.55	0.996
4.60	0.996
4.65	0.996
4.70	0.996
4.75	0.997
4.80	0.997
4.85	0.997
4.90	0.997
4.95	0.997
.>/=5.00	1.000

## METHOD 28A MEASUREMENT OF AIR TO FUEL RATIO AND MINIMUM ACHIEVABLE BURN RATES FOR WOOD-FIRED APPLIANCES

### *1. Applicability and Principle*

1.1 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.

1.2 Principle. 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 percent carbon dioxide (CO[2]), percent oxygen (O[2]), and percent carbon monoxide (CO). These stack gas components are measured for determining dry molecular weight of 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.

### *2. Definitions*

2.1 Burn Rate, Firebox, Secondary Air Supply, Test Facility, Test Fuel Charge, Test Fuel Crib, Test Fuel Loading Density, Test Fuel Piece, Test Run, Usable Firebox Volume, and Wood Heater. Same as Method 28, Sections 2.1 and 2.3 to 2.12.

2.2 Air to Fuel Ratio. 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).

### *3. Apparatus*

3.1 Test Facility. Insulated Solid Pack Chimney, Platform Scale and Monitor, Room Temperature Monitor, Balance, Moisture Meter, Anemometer, Barometer, Draft Gauge, and Humidity Gauge. Same as Method 28, Sections 3.1, 3.2, and 3.4 to 3.10, respectively.

3.2 Sampling System. Probe, Condenser, Valve, Pump, Rate Meter, Flexible Bag, Pressure Gauge, and Vacuum Gauge. Same as Method 3, Sections 2.2.1 to 2.2.8, respectively. The sampling systems described in Method 5H,

Sections 2.2.1, 2.2.2, and 2.2.3, may be used.

3.3 Analysis. Orsat analyzer, same as Method 3, Section 2.3; or instrumental analyzers, same as Method 5H, Sections 2.2.4 and 2.2.5, for CO<sub>2</sub> and CO analyzers, except use a CO analyzer with a range of 0 to 5 percent and use a CO<sub>2</sub> analyzer with a range of 0 to 5 percent. Use an O<sub>2</sub> analyzer capable of providing a measure of O<sub>2</sub> in the range of 0 to 25 percent by volume at least once every 10 minutes. Prepare cylinder gases for the three analyzers as described in Method 5H, Section 3.3.

#### 4. Test Preparation

4.1 Test Facility, Wood Heater Appliance Installation, and Test Facility Conditions. Same as Method 28, Sections 4.1.1 and 4.1.2, respectively, with the exception that barometric dampers or other devices designed to introduce dilution air downstream of the firebox shall be sealed.

4.2 Wood Heater Air Supply Adjustments. 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.

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.

4.2.1 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.

Flue dampers, mechanisms and air inlet ports which could reasonably be expected to be adjusted or closed would include:

- (a) All internal or externally adjustable mechanisms (including adjustments that affect the tightness of door fittings) that are accessible either before and/or after installation.
- (b) 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.
- (c) 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).

(d) 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.

4.2.2 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 (e.g., greatest blockage).

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.

Notwithstanding Section 4.2.1, 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.

4.3 Test Fuel Properties and Test Fuel Charge Specifications. Same as Method 28, Sections 4.2 to 4.3, respectively.

4.4 Sampling System.

4.4.1 Sampling Location. Same as Method 5H, Section 5.1.2.

4.4.2 Sampling System Set Up. Set up the sampling equipment as described in Method 3, Section 3.2, or as in Method 3A, Section 7.

## 5. Procedures

5.1 Pretest Preparation. Same as Method 28, Sections 6.2.1 and 6.2.3 to 6.2.5.

5.2 Pretest Ignition. Same as Method 28, Section 6.3. Set the wood heater air supply settings to achieve a burn rate in Category 1 or the lowest achievable burn rate (see Section 4.2).

5.3 Test Run. Same as Method 28, Section 6.4. Begin sample collection at the start of the test run as defined in Method 28, Section 6.4.1. 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 l per bag is recommended. If instrumental gas concentration measurement procedures are used, conduct the gas measurement system performance specifications checks as described in Method 5H, Sections 6.7, 6.8, and 6.9. The zero drift and calibration drift limits for all three analyzers shall be 0.2 percent O<sub>2</sub>, CO<sub>2</sub>, or CO, as applicable, or less. Other measurement system performance specifications are as defined in Method 5H, Section 4. Sample at a constant rate for the duration of the test run.

5.3.1 Data Recording. Record wood heater operational data, test facility temperature, sample train flow rate, and fuel weight data at 10-minute intervals.

5.3.2 Test Run Completion. Same as Method 28, Section 6.4.6.

5.4 Analysis Procedure.

5.4.1 Method 3 Integrated Bag Samples. Within 4 hours after the sample collection, analyze each bag sample for percent CO<sub>2</sub>, O<sub>2</sub>, and CO using an Orsat analyzer as described in Method 3, Sections 4.2.5 through



4.2.7.

5.4.2 Instrumental Analyzers. Average the percent CO<sub>2</sub>, CO, and O<sub>2</sub> values for the test run.

5.5 Quality Control Procedures.

5.5.1 Data Validation. The following quality control procedure is suggested to provide a check on the quality of the data.

5.5.1.1 Calculate a fuel factor, F<sub>0</sub>, using the following equation:

$$F_0 = (20.9 - \% O_2) / \% CO_2$$

Eq. 28a-4

where:

%O<sub>2</sub> Percent O<sub>2</sub> by volume (dry basis).

%CO<sub>2</sub> Percent CO<sub>2</sub> by volume (dry basis).

20.9 Percent O<sub>2</sub> by volume in ambient air.

If CO is present in quantities measurable by this method, adjust the O<sub>2</sub> and CO<sub>2</sub> values before performing the calculation for F<sub>0</sub> as follows:

$$CO_2 \text{ (adj)} = \% CO_2 + \% CO$$

$$\% O_2 \text{ (adj)} = \% O_2 - 0.5 \% CO$$

where:

%CO = Percent CO by volume (dry basis).

5.5.1.2 Compare the calculated F<sub>0</sub> factor with the expected F<sub>0</sub> range for wood (1.000 - 1.120). Calculated F<sub>0</sub> 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<sub>0</sub> value of 1.05 and calculating a potential range of CO<sub>2</sub> and O<sub>2</sub> values. Acceptance of such results will be based on whether the calculated range includes the exemption limit and the judgment of the administrator.

5.5.1.3 Method 3 Analyses. Compare the results of the analyses of the two bag samples. If all the gas components (O<sub>2</sub>, CO, and CO<sub>2</sub>) values for the two analyses agree within 0.5 percent (e.g., 6.0 percent O<sub>2</sub> for bag 1 and 6.5 percent O<sub>2</sub> for bag 2, agree within 0.5 percent), the results of the bag analyses may be averaged for the calculations in Section 6. 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.

## 6. Calculations

Carry out calculations, retaining at least one extra decimal 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.

## 6.1 Nomenclature.

$M[d]$  = Dry molecular weight, g/g-mole(lb/lb-mole).

$\%CO_2$  = Percent  $CO_2$  by volume (dry basis).

$\%O_2$  = Percent  $O_2$  by volume (dry basis).

$\%CO$  = Percent CO by volume (dry basis).

$\%N_2$  = Percent  $N_2$  by volume (dry basis).

$N[T]$  = Total gram-moles of dry exhaust gas per kg of wood burned (lb-moles/lb).

$Y[CO_2]$  = Measured mole fraction of  $CO_2$  (e.g., 10 percent  $CO_2$  = .10 mole fraction), g/g-mole (lb/lb-mole).

$Y[CO]$  = Measured mole fraction of CO (e.g., 1 percent CO = .01 mole fraction), g/g-mole (lb/lb-mole).

$Y[HC]$  = 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.

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.

42.5 = Gram-moles of carbon in 1 kg of dry wood assuming 51 percent carbon by weight dry basis (.0425 lb/lb).

510 = Grams of carbon in exhaust gas per kg of wood burned.

1,000 = Grams in 1 kg.

6.2 Dry Molecular Weight. Use Equation 28a-1 to calculate the dry molecular weight of the stack gas.

$$M[d] = 0.440(\%CO_2) + 0.320(\%O_2) + 0.280(\%N_2 + \%CO)$$

Eq. 28a-1

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 37.7). A negative error of about 0.4 percent is introduced. The tester may opt to include argon in the analysis using procedures subject to approval of the Administrator.

6.3 Dry Moles of Exhaust Gas. Use Equation 28a-2 to calculate the total moles of dry exhaust gas produced per kilogram of dry wood burned.

$$N[T] = (42.5 / (Y[CO_2] + Y[CO] + Y[HC]))$$

Eq. 28a-2

6.4 Air to Fuel Ratio. Use Equation 28a-3 to calculate the air to fuel ratio on a dry mass basis.

$$A/F = ((N[T] \times M[d] - (510) / (1000))$$

Eq. 28a-3

6.5 Burn Rate. Calculate the fuel burn rate as in Method 28, Section 8.3.

### *7. Bibliography*

Same as Method 3, Section 7, and Method 5H, Section 7.

SOURCE: [36 FR 24877, Dec. 23, 1971]

AUTHORITY: 42 U.S.C. 7401, 7411, 7414, 7416, and 7601.