

Environmental Protection Agency

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Gaseous Organic Sampling and Analysis Data	Date _____
Plant _____	Location _____

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

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

Figure 18-14. Sampling and Analysis Sheet

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A-6 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at www.fdsys.gov.

APPENDIX A-7 TO PART 60—TEST METHODS 19 THROUGH 25E

Method 19—Determination of sulfur dioxide removal efficiency and particulate, sulfur dioxide and nitrogen oxides emission rates
 Method 20—Determination of nitrogen oxides, sulfur dioxide, and diluent emissions from stationary gas turbines
 Method 21—Determination of volatile organic compound leaks
 Method 22—Visual determination of fugitive emissions from material sources and smoke emissions from flares
 Method 23—Determination of Poly-chlorinated Dibenzo-p-Dioxins and Poly-chlorinated Dibenzofurans From Stationary Sources
 Method 24—Determination of volatile matter content, water content, density, volume

solids, and weight solids of surface coatings
 Method 24A—Determination of volatile matter content and density of printing inks and related coatings
 Method 25—Determination of total gaseous nonmethane organic emissions as carbon
 Method 25A—Determination of total gaseous organic concentration using a flame ionization analyzer
 Method 25B—Determination of total gaseous organic concentration using a nondispersive infrared analyzer
 Method 25C—Determination of nonmethane organic compounds (NMOC) in MSW landfill gases
 Method 25D—Determination of the Volatile Organic Concentration of Waste Samples
 Method 25E—Determination of Vapor Phase Organic Concentration in Waste Samples

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

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

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

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

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes

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in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and re-testing with approved methods.

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

METHOD 19—DETERMINATION OF SULFUR DIOXIDE REMOVAL EFFICIENCY AND PARTICULATE MATTER, SULFUR DIOXIDE, AND NITROGEN OXIDE EMISSION RATES**1.0 Scope and Application**

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

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO _x), including:		
Nitric oxide (NO)	10102-43-9	N/A
Nitrogen dioxide (NO ₂)	10102-44-0	N/A
Particulate matter (PM)	None assigned	N/A
Sulfur dioxide (SO ₂)	7499-09-05	N/A

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1.2 Applicability. Where specified by an applicable subpart of the regulations, this method is applicable for the determination of (a) PM, SO₂, and NO_x emission rates; (b) sulfur removal efficiencies of fuel pretreatment and SO₂ control devices; and (c) overall reduction of potential SO₂ emissions.

2.0 Summary of Method

2.1 Emission Rates. Oxygen (O₂) or carbon dioxide (CO₂) concentrations and appropriate F factors (ratios of combustion gas volumes to heat inputs) are used to calculate pollutant emission rates from pollutant concentrations.

2.2 Sulfur Reduction Efficiency and SO₂ Removal Efficiency. An overall SO₂ emission reduction efficiency is computed from the efficiency of fuel pretreatment systems, where applicable, and the efficiency of SO₂ control devices.

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

2.2.2 The SO₂ removal efficiency of a control device is determined by measuring the SO₂ rates before and after the control device.

2.2.2.1 The inlet rates to SO₂ control systems (or, when SO₂ control systems are not used, SO₂ emission rates to the atmosphere) are determined by fuel sampling and analysis.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety [Reserved]

6.0 Equipment and Supplies [Reserved]

7.0 Reagents and Standards [Reserved]

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

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedures [Reserved]

12.0 Data Analysis and Calculations

12.1 Nomenclature

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

E_{di} = Average inlet SO₂ rate for each sampling period d, ng/J (lb/million Btu)

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

E_{ga} = Daily geometric average pollutant rate, ng/J (lbs/million Btu) or ppm corrected to 7 percent O₂.

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 O₂.

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

E_{hj} = Hourly arithmetic average pollutant rate for hour "j," ng/J (lb/million Btu) or ppm corrected to 7 percent O₂.

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

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

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

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

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

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

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

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

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%H₂O = Concentration of water from an ultimate analysis of fuel, weight percent.

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

K = Conversion factor, 10⁻⁵ (kJ/J)(%) [10³ Btu/million Btu].

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

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

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

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

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

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

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

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

ln = Natural log of indicated value.

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

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

N = Number of fuel lots during the averaging period.

n = Number of fuels being burned in combination.

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

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

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

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

P_s = Potential SO₂ emissions, percent.

%R_f = SO₂ removal efficiency from fuel pretreatment, percent.

%R_g = SO₂ removal efficiency of the control device, percent.

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

%R_o = Overall SO₂ reduction, percent.

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

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

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

S_i = Standard deviation of the hourly average inlet pollutant rates for each per-

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formance test period, ng/J (lb/million Btu).

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

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

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

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

12.2 Emission Rates of PM, SO₂, and NO_x. Select from the following sections the applicable procedure to compute the PM, SO₂, or NO_x emission rate (E) in ng/J (lb/million Btu). The pollutant concentration must be in ng/scm (lb/scf) and the F factor must be in scm/J (scf/million Btu). If the pollutant concentration (C) is not in the appropriate units, use Table 19-1 in section 17.0 to make the proper conversion. An F factor is the ratio of the gas volume of the products of combustion to the heat content of the fuel. The dry F factor (F_d) includes all components of combustion less water, the wet F factor (F_w) includes all components of combustion, and the carbon F factor (F_c) includes only carbon dioxide.

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

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

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

12.2.2 Oxygen-Based F Factor, Wet Basis. When measurements are on a wet basis for both O₂ (%O_{2w}) and pollutant (C_w) concentrations, use either of the following:

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

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

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

NOTE: The estimates are selected to ensure that negative errors will not be larger than -1.5 percent. However, positive errors, or

over-estimation of emissions by as much as 5 percent may be introduced depending upon the geographic location of the facility and the associated range of ambient moisture.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

12.3 F Factors. Use an average F factor according to section 12.3.1 or determine an applicable F factor according to section 12.3.2. If combined fuels are fired, prorate the appli-

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cable F factors using the procedure in section 12.3.3.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

12.4 Determination of Average Pollutant Rates.

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

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

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

$$E_a = \frac{\sum_{j=1}^D (n_j E_{dj})}{\sum_{j=1}^D n_{dj}} \quad \text{Eq. 19-20}$$

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

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

12.5 Determination of Overall Reduction in Potential Sulfur Dioxide Emission.

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

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

12.5.2 Pretreatment Removal Efficiency (Optional). Compute the SO_2 removal efficiency from fuel pretreatment ($\%R_f$) for the

averaging period (e.g., 90 days) as specified in the applicable regulation using the following equation:

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

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

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

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

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

12.5.2.1.2 ASTM Lot Size. For the purpose of section 12.5.2 (fuel pretreatment), the lot size of product coal is the weight of product coal from one type of raw coal. The lot size of raw coal is the weight of raw coal used to produce one lot of product coal. Typically, the lot size is the weight of coal processed in a 1-day (24-hour) period. If more than one type of coal is treated and produced in 1 day,

then gross samples must be collected and analyzed for each type of coal. A coal lot size equaling the 90-day quarterly fuel quantity for a steam generating unit may be used if representative sampling can be conducted for each raw coal and product coal.

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

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

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

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

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

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

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

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

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

$$K = 2 \times 10^7 \left(\frac{\text{ng SO}_2}{\%S} \right) \left(\frac{(\text{kJ})}{\text{J}} \right) \left(\frac{1}{\text{kg coal}} \right) \left[2 \times 10^4 \left(\frac{\text{lb SO}_2}{\%S} \right) \left(\frac{\text{Btu}}{\text{million Btu}} \right) \left(\frac{1}{\text{lb coal}} \right) \right]$$

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

12.5.3.2 Collect the fuel samples from a location in the fuel handling system that provides a sample representative of the fuel bunkered or consumed during a steam generating unit operating day. For the purpose of as-fired fuel sampling under section 12.5.3.2 or section 12.6, the lot size for coal is the weight of coal bunkered or consumed during each steam generating unit operating day. The lot size for oil is the weight of oil supplied to the "day" tank or consumed during each steam generating unit operating day. For reporting and calculation purposes, the gross sample shall be identified with the calendar day on which sampling began. For steam generating unit operating days when a

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

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

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

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

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

Where:

coal-fired steam generating unit is operated without coal being added to the bunkers, the coal analysis from the previous "as bunkered" coal sample shall be used until coal is bunkered again. For steam generating unit operating days when an oil-fired steam generating unit is operated without oil being added to the oil "day" tank, the oil analysis from the previous day shall be used until the "day" tank is filled again. Alternative definitions of fuel lot size may be used, subject to prior approval of the Administrator.

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

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

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

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

12.6 Sulfur Retention Credit for Compliance Fuel. If fuel sampling and analysis procedures in section 12.5.2.1 are being used to determine average SO₂ emission rates (E_{ao}) to the atmosphere from a coal-fired steam generating unit when there is no SO₂ control de-

vise, the following equation may be used to adjust the emission rate for sulfur retention credits (no credits are allowed for oil-fired systems) (E_{di}) for each sampling period using the following equation:

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

Where:

$$K = 2 \times 10^7 \left(\frac{\text{ng SO}_2}{\%S} \right) \left(\frac{\text{kJ}}{\text{J}} \right) \left(\frac{1}{\text{kg coal}} \right) \left[2 \times 10^4 \left(\frac{\text{lb SO}_2}{\%S} \right) \left(\frac{\text{Btu}}{\text{million Btu}} \right) \left(\frac{1}{\text{lb coal}} \right) \right]$$

After calculating E_{di}, use the procedures in section 12.4.2 to determine the average SO₂ emission rate to the atmosphere for the performance test period (E_{ao}).

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

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

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

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

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

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

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

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

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

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

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 19-1—CONVERSION FACTORS FOR CONCENTRATION

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

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TABLE 19-1—CONVERSION FACTORS FOR CONCENTRATION—Continued

From	To	Multiply by
ppm SO ₂	ng/scm	2.66×10^6
ppm NO _x	ng/scm	1.912×10^6
ppm SO ₂	lb/scf	1.660×10^{-7}
ppm NO _x	lb/scf	1.194×10^{-7}

TABLE 19-2—F FACTORS FOR VARIOUS FUELS¹

¹ Determined at standard conditions: 20 °C (68 °F) and 760 mm Hg (29.92 in Hg).

² As classified according to ASTM D 388.

³ Crude, residual, or distillate.

TABLE 19-3—VALUES FOR $T_{0.95}$

n ¹	t _{0.95}	n ¹	t _{0.95}	n ¹	t _{0.95}
2	6.31	8	1.89	22-26	1.7
3	2.42	9	1.86	27-31	1.7
4	2.35	10	1.83	32-51	1.6
5	2.13	11	1.81	52-91	1.6
6	2.02	12-16	1.77	92-151	1.6
7	1.94	17-21	1.73	152 or more	1.6

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

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

1.0 Scope and Application

What is Method 20?

Method 20 contains the details you must follow when using an instrumental analyzer to determine concentrations of nitrogen ox-

ides, oxygen, carbon dioxide, and sulfur dioxide in the emissions from stationary gas turbines. This method follows the specific instructions for equipment and performance requirements, supplies, sample collection and analysis, calculations, and data analysis in the methods listed in section 2.0.

1.1 Analytes. What does this method determine?

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

1.2 Applicability. When is this method required? The use of Method 20 may be required by specific New Source Performance Standards, Clean Air Marketing rules, and State

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measuring SO₂, NO_x, CO₂, and/or O₂ concentrations in stationary gas turbines emissions are required. Other regulations may also require its use.

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

2.0 Summary of Method

In this method, NO_x, O₂ (or CO₂), and SO_x are measured using the following methods found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 3A—Determination of Oxygen and Carbon Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).
- (c) Method 6C—Determination of Sulfur Dioxide Emissions From Stationary Sources (Instrumental Analyzer Procedure).
- (d) Method 7E—Determination of Nitrogen Oxides Emissions From Stationary Sources (Instrumental Analyzer Procedure).
- (e) Method 19—Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide, and Nitrogen Oxide Emission Rates.

3.0 Definitions

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

4.0 Interferences

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

5.0 Safety

Refer to section 5.0 of Method 7E.

6.0 Equipment and Supplies

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

7.0 Reagents and Standards

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

8.0 Sample Collection, Preservation, Storage, and Transport

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

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

8.3 Interference Check. You must follow the procedures in section 8.3 of Method 3A or 6C.

or section 8.2.7 of Method 7E (as appropriate).

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

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

9.0 Quality Control

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

10.0 Calibration and Standardization

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

11.0 Analytical Procedures

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

12.0 Calculations and Data Analysis

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

13.0 Method Performance

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

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

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

17.0 References

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

18.0 Tables, Diagrams, Flowcharts, and Validation Data

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

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1.0 Scope and Application

1.1 Analytes

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

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

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

2.0 Summary of Method

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

3.0 Definitions

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

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

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

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

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

leak. In this example, the leak definition concentration is 10,000 ppm and the reference compound is methane.)

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

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

4.0 Interferences [Reserved]**5.0 Safety**

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

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

6.0 Equipment and Supplies

A VOC monitoring instrument meeting the following specifications is required:

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

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

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

6.4 The instrument shall be equipped with an electrically driven pump to ensure that a sample is provided to the detector at a constant flow rate. The nominal sample flow rate, as measured at the sample probe tip, shall be 0.10 to 3.0 l/min (0.004 to 0.1 ft³/min) when the probe is fitted with a glass wool plug or filter that may be used to prevent plugging of the instrument.

6.5 The instrument shall be equipped with a probe or probe extension or sampling not to exceed 6.4 mm ($\frac{1}{4}$ in) in outside diameter.

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with a single end opening for admission of sample.

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

7.0 Reagents and Standards

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

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

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

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

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

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

8.0 Sample Collection, Preservation, Storage, and Transport

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

8.1.1 Response Factor. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

8.1.1.1 Calibrate the instrument with the reference compound as specified in the applicable regulation. Introduce the calibration gas mixture to the analyzer and record the observed meter reading. Introduce zero gas until a stable reading is obtained. Make a total of three measurements by alternating between the calibration gas and zero gas. Calculate the response factor for each repetition and the average response factor.

8.1.1.2 The instrument response factors for each of the individual VOC to be measured shall be less than 10 unless otherwise specified in the applicable regulation. When no instrument is available that meets this specification when calibrated with the reference VOC specified in the applicable regulation, the available instrument may be calibrated with one of the VOC to be measured, or any other VOC, so long as the instrument then has a response factor of less than 10 for each of the individual VOC to be measured.

8.1.1.3 Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in References 1-3 of section 17.0.

8.1.2 Calibration Precision. The calibration precision test must be completed prior to placing the analyzer into service and at subsequent 3-month intervals or at the next use, whichever is later.

8.1.2.1 Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

8.1.2.2 The calibration precision shall be equal to or less than 10 percent of the calibration gas value.

8.1.3 Response Time. The response time test is required before placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

8.1.3.1 Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. After switching, measure the time required to attain 90 percent of the final stable reading. Perform this test sequence three times and record the results. Calculate the average response time.

8.1.3.2 The instrument response time shall be equal to or less than 30 seconds. The instrument pump, dilution probe (if any), sample probe, and probe filter that will be used

during testing shall all be in place during the response time determination.

8.2 Instrument Calibration. Calibrate the VOC monitoring instrument according to section 10.0.

8.3 Individual Source Surveys.

8.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

8.3.1.1 Valves. The most common source of leaks from valves is the seal between the stem and housing. Place the probe at the interface where the stem exits the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

8.3.1.2 Flanges and Other Connections. For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

8.3.1.3 Pumps and Compressors. Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

8.3.1.4 Pressure Relief Devices. The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

8.3.1.5 Process Drains. For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

8.3.1.6 Open-ended Lines or Valves. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.7 Seal System Degassing Vents and Accumulator Vents. Place the probe inlet at approximately the center of the opening to the atmosphere.

8.3.1.8 Access door seals. Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

8.3.2 Type II—"No Detectable Emission". Determine the local ambient VOC concentration around the source by moving the probe randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration as outlined in section 8.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation. For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

8.3.2.1 Pump or Compressor Seals. If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described in section 8.3.2.

8.3.2.2 Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices. If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur upstream of the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere upstream of the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in section 8.3.2 shall be used to determine if detectable emissions exist.

8.3.3 Alternative Screening Procedure.

8.3.3.1 A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open

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areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument technique of section 8.3.1 or 8.3.2.

8.3.3.2 Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure

sprayer or squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of section 8.3.1 or 8.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Instrument calibration precision check	Ensure precision and accuracy, respectively, of instrument response to standard.
10.0	Instrument calibration.	

10.0 Calibration and Standardization

10.1 Calibrate the VOC monitoring instrument as follows. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE: If the meter readout cannot be adjusted to the proper value, a malfunction of the analyzer is indicated and corrective actions are necessary before use.

11.0 Analytical Procedures [Reserved]**12.0 Data Analyses and Calculations [Reserved]****13.0 Method Performance [Reserved]****14.0 Pollution Prevention [Reserved]****15.0 Waste Management [Reserved]****16.0 References**

1. Dubose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2-81051. September 1981.

2. Brown, G.E., et al. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2-81-022. May 1981.

3. DuBose, D.A. et al. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA 600/2-81-110. September 1981.

4. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]**METHOD 22—VISUAL DETERMINATION OF FUGITIVE EMISSIONS FROM MATERIAL SOURCES AND SMOKE EMISSIONS FROM FLARES**

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from Method 9.

1.0 Scope and Application

This method is applicable for the determination of the frequency of fugitive emissions from stationary sources, only as specified in an applicable subpart of the regulations. This method also is applicable for the determination of the frequency of visible smoke emissions from flares.

2.0 Summary of Method

2.1 Fugitive emissions produced during material processing, handling, and transfer operations or smoke emissions from flares are visually determined by an observer without the aid of instruments.

2.2 This method is used also to determine visible smoke emissions from flares used for combustion of waste process materials.

2.3 This method determines the amount of time that visible emissions occur during the observation period (*i.e.*, the accumulated emission time). This method does not require that the opacity of emissions be determined. Since this procedure requires only the determination of whether visible emissions occur and does not require the determination of opacity levels, observer certification according to the procedures of Method 9 is not required. However, it is necessary that the observer is knowledgeable with respect to the general procedures for determining the presence of visible emissions. At a minimum, the observer must be trained and knowledgeable regarding the effects of background contrast, ambient lighting, observer position relative

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to lighting, wind, and the presence of uncombined water (condensing water vapor) on the visibility of emissions. This training is to be obtained from written materials found in References 1 and 2 or from the lecture portion of the Method 9 certification course.

3.0 Definitions

3.1 *Emission frequency* means the percentage of time that emissions are visible during the observation period.

3.2 *Emission time* means the accumulated amount of time that emissions are visible during the observation period.

3.3 *Fugitive emissions* means emissions generated by an affected facility which is not collected by a capture system and is released to the atmosphere. This includes emissions that (1) escape capture by process equipment exhaust hoods; (2) are emitted during material transfer; (3) are emitted from buildings housing material processing or handling equipment; or (4) are emitted directly from process equipment.

3.4 *Observation period* means the accumulated time period during which observations are conducted, not to be less than the period specified in the applicable regulation.

3.5 *Smoke emissions* means a pollutant generated by combustion in a flare and occurring immediately downstream of the flame. Smoke occurring within the flame, but not downstream of the flame, is not considered a smoke emission.

4.0 Interferences

4.1 Occasionally, fugitive emissions from sources other than the affected facility (e.g., road dust) may prevent a clear view of the affected facility. This may particularly be a problem during periods of high wind. If the view of the potential emission points is obscured to such a degree that the observer questions the validity of continuing observations, then the observations shall be terminated, and the observer shall clearly note this fact on the data form.

5.0 Safety

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

6.0 Equipment

6.1 Stopwatches (two). Accumulative type with unit divisions of at least 0.5 seconds.

6.2 Light Meter. Light meter capable of measuring illuminance in the 50 to 200 lux range, required for indoor observations only.

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7.0 Reagents and Supplies [Reserved]

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

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Selection of Observation Location. Survey the affected facility, or the building or structure housing the process to be observed, and determine the locations of potential emissions. If the affected facility is located inside a building, determine an observation location that is consistent with the requirements of the applicable regulation (i.e., outside observation of emissions escaping the building/structure or inside observation of emissions directly emitted from the affected facility process unit). Then select a position that enables a clear view of the potential emission point(s) of the affected facility or of the building or structure housing the affected facility, as appropriate for the applicable subpart. A position at least 4.6 m (15 feet), but not more than 400 m (0.25 miles), from the emission source is recommended. For outdoor locations, select a position where the sunlight is not shining directly in the observer's eyes.

11.2 Field Records.

11.2.1 Outdoor Location. Record the following information on the field data sheet (Figure 22-1): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record also the estimated wind speed, wind direction, and sky condition. Sketch the process unit being observed, and note the observer location relative to the source and the sun. Indicate the potential and actual emission points on the sketch.

11.2.2 Indoor Location. Record the following information on the field data sheet (Figure 22-2): Company name, industry, process unit, observer's name, observer's affiliation, and date. Record as appropriate the type, location, and intensity of lighting on the data sheet. Sketch the process unit being observed, and note the observer location relative to the source. Indicate the potential and actual fugitive emission points on the sketch.

11.3 Indoor Lighting Requirements. For indoor locations, use a light meter to measure the level of illumination at a location as close to the emission source(s) as is feasible. An illumination of greater than 100 lux (10 foot candles) is considered necessary for proper application of this method.

11.4 Observations.

11.4.1 Procedure. Record the clock time when observations begin. Use one stopwatch to monitor the duration of the observation

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period. Start this stopwatch when the observation period begins. If the observation period is divided into two or more segments by process shutdowns or observer rest breaks (see section 11.4.3), stop the stopwatch when a break begins and restart the stopwatch without resetting it when the break ends. Stop the stopwatch at the end of the observation period. The accumulated time indicated by this stopwatch is the duration of observation period. When the observation period is completed, record the clock time. During the observation period, continuously watch the emission source. Upon observing an emission (condensed water vapor is not considered an emission), start the second accumulative stopwatch; stop the watch when the emission stops. Continue this procedure for the entire observation period. The accumulated elapsed time on this stopwatch is the total time emissions were visible during the observation period (i.e., the emission time.)

11.4.2 Observation Period. Choose an observation period of sufficient length to meet the requirements for determining compliance with the emission standard in the applicable subpart of the regulations. When the length of the observation period is specifically stated in the applicable subpart, it may not be necessary to observe the source for this entire period if the emission time required to indicate noncompliance (based on the specified 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 emission are observed since 6 minutes is 10 percent of an hour. In any case, the observation period shall not be less than 6 minutes in duration. In some cases, the process operation may be intermittent or cyclic. In such cases, it may be convenient for the observation period to coincide with the length of the process cycle.

11.4.3 Observer Rest Breaks. Do not observe emissions continuously for a period of more

than 15 to 20 minutes without taking a rest break. For sources requiring observation periods of greater than 20 minutes, the observer shall take a break of not less than 5 minutes and not more than 10 minutes after every 15 to 20 minutes of observation. If continuous observations are desired for extended time periods, two observers can alternate between making observations and taking breaks.

11.5 Recording Observations. Record the accumulated time of the observation period on the data sheet as the observation period duration. Record the accumulated time emissions were observed on the data sheet as the emission time. Record the clock time the observation period began and ended, as well as the clock time any observer breaks began and ended.

12.0 Data Analysis and Calculations

If the applicable subpart requires that the emission rate be expressed as an emission frequency (in percent), determine this value as follows: Divide the accumulated emission time (in seconds) by the duration of the observation period (in seconds) or by any minimum observation period required in the applicable subpart, if the actual observation period is less than the required period, and multiply this quotient by 100.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. EPA Publication No. EPA-340/1-75-007, April 1975.

2. Wohlschlegel, P., and D.E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emissions from Stationary Sources, EPA Publication No. EPA-650/4-74-005i. November 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

FUGITIVE OR SMOKE EMISSION INSPECTION OUTDOOR LOCATION			
Company Location Company Rep.	Observer Affiliation Date		
Sky Conditions Precipitation	Wind Direction Wind Speed		
Industry	Process Unit		
Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.			
OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin Observation	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
End Observation	_____	_____	_____
	_____	_____	_____

Figure 22-1

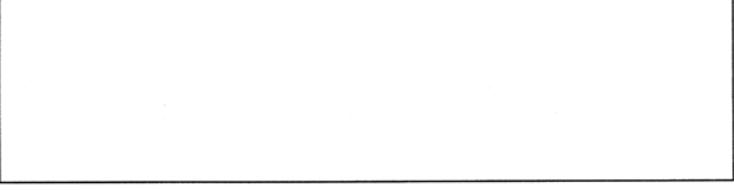
FUGITIVE OR SMOKE EMISSION INSPECTION INDOOR LOCATION			
Company Location Company Rep.	Observer Affiliation Date		
Industry	Process Unit		
Light type (fluorescent, incandescent, natural) Light location (overhead, behind observer, etc.) Illuminance (lux or footcandles) Sketch process unit: indicate observer position relative to source; indicate potential emission points and/or actual emission points.			
			
OBSERVATIONS	Clock Time	Observation period duration, min:sec	Accumulated emission time, min:sec
Begin	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
End Observation	_____	_____	_____

Figure 22-2

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and poly-

chlorinated 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:

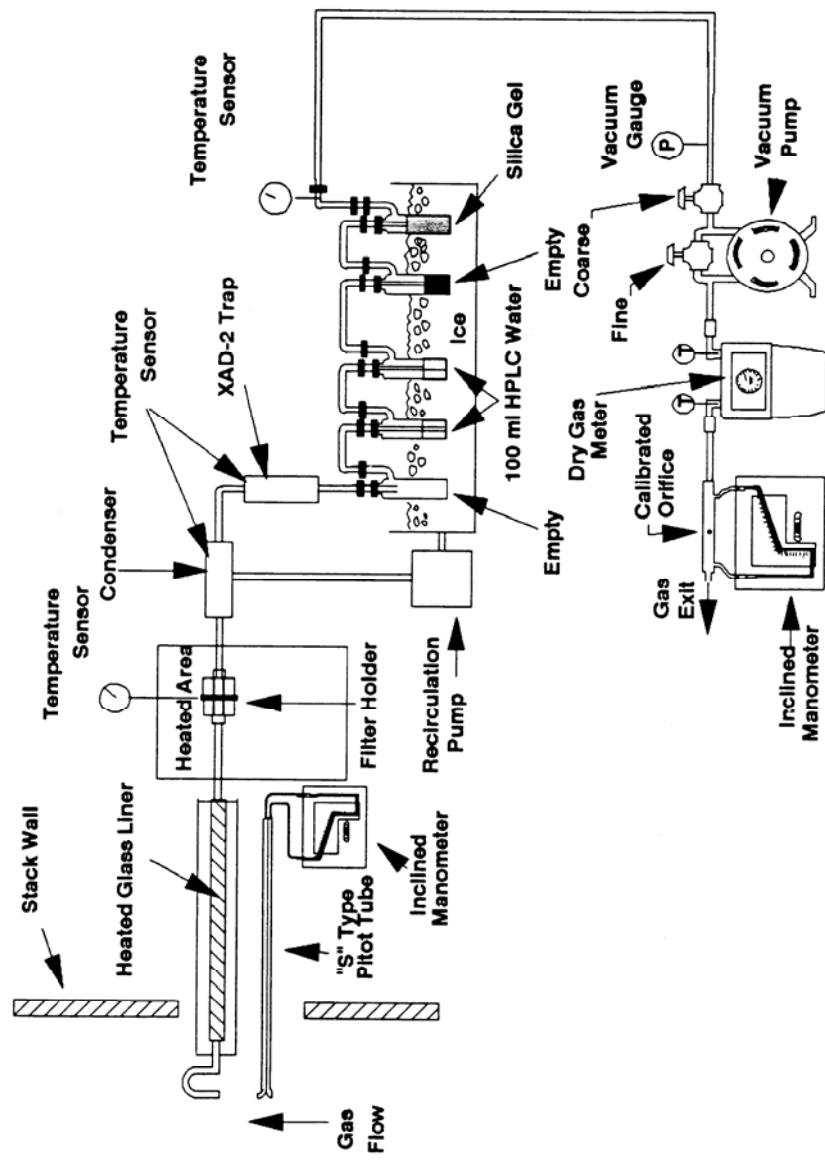


Figure 23.1 Sampling train

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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 ($\frac{1}{2}$ in. OD with $\frac{1}{8}$ 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 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23-2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic dia-

gram is shown in Figure 23-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner, Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

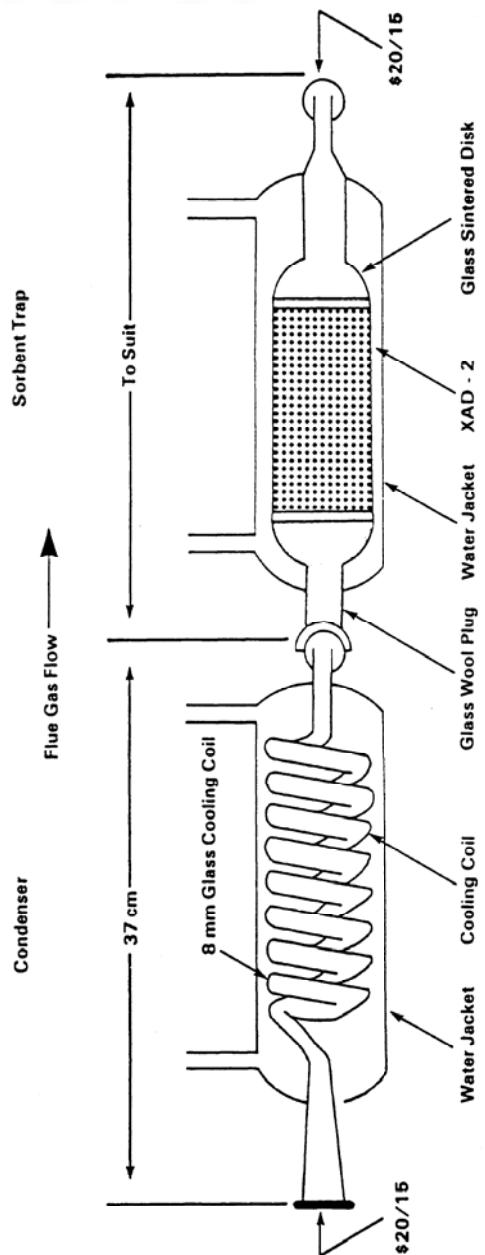


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

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- 2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.
- 2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.
- 2.3 Analysis.
- 2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.
- 2.3.2 Test Tube. Glass.
- 2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.
- 2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.
- 2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.
- 2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.
- 2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.
- 2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.
- 2.3.9 Separatory Funnels. Glass, 2-liter.
- 2.3.10 Gas Chromatograph. Consisting of the following components:
- 2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature $\pm^{\circ}\text{C}$ and performing programmed increases in temperature at rates of at least $40\ ^{\circ}\text{C}/\text{min}$.
- 2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures $\pm^{\circ}\text{C}$.
- 2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.
- 2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m × 0.25 mm ID coated with DB-225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.
- 2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ± 5 ppm.
- 2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.
- 2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD-2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order:

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over $40\ ^{\circ}\text{C}$. 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.

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3.1.2.3.2 Analysis. Inject a 2 μ l sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft \times $\frac{1}{4}$ in stainless steel containing 10 percent OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 μ l of methylene chloride into 100 ml of toluene. This corresponds to 100 μ g of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μ 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 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

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

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.1 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.

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3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a 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

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isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 µl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD-0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed

silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23-1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by

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brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

5. Analysis

All glassware shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle con-

taining 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 Methylen Chloride). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 μ 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 $\frac{1}{2}$ 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 μ 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 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

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5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX-21 Carbon/Celite 545 Column. Remove the 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/ceelite 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/ceelite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N₂. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each

isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8-tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2M + 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 ¹³C-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 ¹³C-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 PCDFE 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 ¹³C₁₂-2,3,7,8-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 $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on μl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 μl of the surrogate standards in Table 1 to the 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.

8.0 [Reserved]

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the j th calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the j th calibration standard.

A_{sci} = 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_r = Integrated ion current of the two ions characteristic of the recovery standard.

A_s = 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 .

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C_T = Total concentration of PCDD's or PCDF's in the sample, pg/M³.
 m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
 m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
 m_{si} = Mass of surrogate compound in the calibration standard, pg.
 RRF_i = Relative response factor.
 RRF_{rs} = Recovery standard response factor.
 RRF_s = Surrogate compound response factor.
 9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n} \sum_{j=1}^n \frac{A_{cij} m_{ci}^*}{A_{cij}^* m_{ci}} \quad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{\text{mstd}}} \quad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs} m_{ci}^*} \quad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RRF_{rs} m_i^*} \times 100\% \quad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^* m_s}{A_{cis} m_{ci}^*} \quad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \quad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5 A_{ai} m_i^*}{A_{ci}^* RRF_i} \quad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^n C_i \quad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

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Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington DC. December 1984. 25 p.

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/ μ 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-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/ μ 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

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TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
Recovery Standards: ¹³ C ₁₂ -1,2,3,4-TCDD ..	100	100	100	100	100

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS—Continued

Compound	Concentrations (pg/μL)				
	Solution No.				
	1	2	3	4	5
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD ..	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C ₀ F ₁₁	PFK
	303.9016	M	C ₁ H ₃₅ Cl ₄ O	TCDF
	305.8987	M + 2	C ₁ H ₃₅ Cl ³⁷ O	TCDF
	315.9419	M	¹³ C ₁ H ₃₅ Cl ₄ O	TCDF (S)
	317.9389	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO	TCDF (S)
	319.8965	M	C ₁ H ₃₅ ClO ₂	TCDD
	321.8936	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO ₂	TCDD
	327.8847	M	C ₁ H ₃₇ Cl ₄ O ₂	TCDD (S)
	330.9792	QC	C ₀ F ₁₃	PFK
	331.9368	M	¹³ C ₁ H ₃₅ Cl ₄ O ₂	TCDD (S)
	333.9339	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO ₂	TCDD (S)
	339.8597	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO	PeCDF
	341.8567	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	PeCDF
	351.9000	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO	PeCDF (S)
	353.8970	M + 4	¹³ C ₁ H ₃₅ Cl ₃₅ Cl ₃₇ Cl ₂ O	PeCDF (S)
	355.8546	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO ₂	PeCDD
	357.8516	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	PeCDD
	367.8949	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO ₂	PeCDD (S)
	369.8919	M + 4	¹³ C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	PeCDD (S)
	375.8364	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO	HxCDF
	409.7974	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO	HxCDF
	373.8208	M + 2	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	HxCDF
	375.8178	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	HxCDF
	383.8639	M	¹³ C ₁ H ₃₅ Cl ₄ O	HxCDF (S)
	385.8610	M + 2	¹³ C ₁ H ₃₅ Cl ₃₅ Cl ₃₇ ClO	HxCDF (S)
	389.8157	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO ₂	HxCDD
	391.8127	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	HxCDD
	392.9760	LOCK	C ₀ F ₁₅	PFK
	401.8559	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO ₂	HxCDD (S)
	403.8529	M + 4	¹³ C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	HxCDD (S)
	445.7555	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	OCDFE
	430.9729	QC	C ₀ F ₁₇	PFK
4	407.7818	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO	HxCDF
	409.7789	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	HxCDF
	417.8253	M	¹³ C ₁ H ₃₅ Cl ₄ O	HxCDF (S)
	419.8220	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO	HxCDF (S)
	423.7766	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO ₂	HxCDD
	425.7737	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	HxCDD
	435.8169	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO ₂	HxCDD (S)
	437.8140	M + 4	¹³ C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	HxCDD (S)
	479.7165	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	NCPDE
	430.9729	LOCK	C ₀ F ₁₇	PFK
	441.7428	M + 2	C ₁ H ₃₅ Cl ₃₇ ClO	OCDF
	443.7399	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O	OCDF
	457.7377	M + 2	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	OCDD
	459.7348	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	OCDD
	469.7778	M + 2	¹³ C ₁ H ₃₅ Cl ₃₇ ClO ₂	OCDD (S)
	471.7750	M + 4	¹³ C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	OCDD (S)
	513.6775	M + 4	C ₁ H ₃₅ Cl ₃₇ Cl ₂ O ₂	DCDPE
	442.9728	QC	C ₀ F ₁₇	PFK

(a) The following nuclidic masses were used:

H = 1.007825

C = 12.000000

¹³C = 13.003355

F = 18.9984

O = 15.994915

³⁵Cl = 34.968853

³⁷Cl = 36.965903

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S = Labeled Standard

QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6 ^a	M/M + 2	0.51	0.43	0.59
7 ^b	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

^a Used only for ¹³C-HxCDF.

^b Used only for ¹³C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
1,2,3,4,6,7,8-HxCDF	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-HpCDF	30	30
¹³ C ₁₂ -OCDD	30	30
¹³ C ₁₂ -2,3,7,8-TCDF	30	30
¹³ C ₁₂ -1,2,3,7,8-PeCDF	30	30
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	30	30
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
³⁷ Cl ₄ -2,3,7,8-TCDD	25	25
¹³ C ₁₂ -2,3,4,7,8-PeCDF	25	25
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	25	25
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	25	25
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS
1.0 Scope and Application
1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds Water.	No CAS Number assigned 7732-18-5

1.2 Applicability. This method is applicable for the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

1.3 Precision and Bias. Intra-and inter-laboratory analytical precision statements are presented in section 13.1. No bias has been identified.

2.0 Summary of Method

2.1 Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or other related surface coatings.

3.0 Definitions

3.1 *Waterborne coating* means any coating which contains more than 5 percent water by weight in its volatile fraction.

3.2 *Multicomponent coatings* are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating.

3.3 *Ultraviolet (UV) radiation-cured coatings* are coatings which contain unreacted monomers that are polymerized by exposure to ultraviolet light.

4.0 Interferences [Reserved]
5.0 Safety

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

5.2 Hazardous Components. Several of the compounds that may be contained in the coatings analyzed by this method may be irritating or corrosive to tissues (e.g., heptane) or may be toxic (e.g., benzene, methyl alcohol). Nearly all are fire hazards.

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Appropriate precautions can be found in reference documents, such as Reference 3 of section 16.0.

6.0 Equipment and Supplies

The equipment and supplies specified in the ASTM methods listed in sections 6.1 through 6.6 (incorporated by reference—see § 60.17 for acceptable versions of the methods) are required:

6.1 ASTM D 1475-60, 80, or 90, Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products.

6.2 ASTM D 2369-81, 87, 90, 92, 93, or 95, Standard Test Method for Volatile Content of Coatings.

6.3 ASTM D 3792-79 or 91, Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph.

6.4 ASTM D 4017-81, 90, or 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method.

6.5 ASTM 4457-85 91, Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.

6.6 ASTM D 5403 93, Standard Test Methods for Volatile Content of Radiation Curable Materials.

6.7 ASTM D 6419-00, Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks.

7.0 Reagents and Standards

7.1 The reagents and standards specified in the ASTM methods listed in sections 6.1 through 6.6 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 1 of section 16.0.

9.0 Quality Control

9.1 Reproducibility

NOTE: Not applicable to UV radiation-cured coatings. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. Verification is accomplished by running duplicate analyses on each sample tested (Sections 11.2 through 11.4) and comparing the results with the intra-laboratory precision statements (Section 13.1) for each parameter.

9.2 Confidence Limits for Waterborne Coatings. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent of water increases, measured param-

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eters for waterborne coatings are replaced with appropriate confidence limits (Section 12.6). These confidence limits are based on measured parameters and inter-laboratory precision statements.

10.0 Calibration and Standardization

10.1 Perform the calibration and standardization procedures specified in the ASTM methods listed in sections 6.1 through 6.6.

11.0 Analytical Procedure

Additional guidance can be found in Reference 2 of section 16.0.

11.1 Non Thin-film Ultraviolet Radiation-cured (UV radiation-cured) Coatings.

11.1.1 Volatile Content. Use the procedure in ASTM D 5403 to determine the volatile matter content of the coating except the curing test described in NOTE 2 of ASTM D 5403 is required.

11.1.2 Water Content. To determine water content, follow section 11.3.2.

11.1.3 Coating Density. To determine coating density, follow section 11.3.3.

11.1.4 Solids Content. To determine solids content, follow section 11.3.4.

11.1.5 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the equation in section 12.2. If C is less than 0.2 g and A is greater than or equal to $225 \text{ cm}^2 (35 \text{ in}^2)$ then the coating or ink is considered a thin-film UV radiation-cured coating and ASTM D 5403 is not applicable.

NOTE: As noted in section 1.4 of ASTM D 5403, this method may not be applicable to radiation curable materials wherein the volatile material is water.

11.2 Multi-component Coatings.

11.2.1 Sample Preparation.

11.2.1.1 Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by section 11.3.3.

11.2.1.2 Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, and density.

11.2.2 Volatile Content. To determine total volatile content, use the apparatus and

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reagents described in ASTM D2369 (incorporated by reference; see §60.17 for the approved versions of the standard), respectively, and use the following procedures:

11.2.2.1 Weigh and record the weight of an aluminum foil weighing dish. Add 3 ± 1 ml of suitable solvent as specified in ASTM D2369 to the weighing dish. Using a syringe as specified in ASTM D2369, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is $0.3 + 0.10$ g, but for coatings believed to have a volatile content greater than 40 weight percent, a suitable size is 0.5 ± 0.1 g.

NOTE: If the volatile content determined pursuant to section 12.4 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for a minimum of 1 hour, but no more than 24 hours prior to being oven cured at 110 ± 5 °C (230 ± 9 °F) for 1 hour.

11.2.2.2 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 min at 110 ± 5 °C (230 ± 9 °F). Caution—provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

11.2.2.3 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to within 1 mg.

11.2.2.4 Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in section 11.4 is met. Calculate W_v following Equation 24-2 and record the arithmetic average.

11.2.3 Water Content. To determine water content, follow section 11.3.2.

11.2.4 Coating Density. To determine coating density, follow section 11.3.3.

11.2.5 Solids Content. To determine solids content, follow section 11.3.4.

11.2.6 Exempt Solvent Content. To determine the exempt solvent content, follow section 11.3.5.

NOTE: For all other coatings (*i.e.*, water- or solvent-borne coatings) not covered by multicomponent or UV radiation-cured coatings, analyze as shown below:

11.3 Water- or Solvent-borne coatings.

11.3.1 Volatile Content. Use the procedure in ASTM D 2369 to determine the volatile matter content (may include water) of the coating.

11.3.1.1 Record the following information:

W_1 = weight of dish and sample before heating, g

W_2 = weight of dish and sample after heating, g

W_3 = sample weight, g.

11.3.1.2 Calculate the weight fraction of the volatile matter (W_v) for each analysis as shown in section 12.3.

11.3.1.3 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.1.4 Record the arithmetic average (W_v).

11.3.2 Water Content. For waterborne coatings only, determine the weight fraction of water (W_w) using either ASTM D 3792 or ASTM D 4017.

11.3.2.1 Run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement in section 13.1.

11.3.2.2 Record the arithmetic average (W_w).

11.3.3 Coating Density. Determine the density (D_c , kg/l) of the surface coating using the procedure in ASTM D 1475.

11.3.3.1 Run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement in section 13.1.

11.3.3.2 Record the arithmetic average (D_c).

11.3.4 Solids Content. Determine the volume fraction (V_s) of the coating by calculation using the manufacturer's formulation.

11.3.5 Exempt Solvent Content. Determine the weight fraction of exempt solvents (W_E) by using ASTM Method D4457. Run a duplicate set of determinations and record the arithmetic average (W_E).

11.4 Sample Analysis Criteria. For W_v and W_w , run duplicate analyses until the difference between the two values in a set is less than or equal to the intra-laboratory precision statement for that parameter. For D_c , run duplicate analyses until each value in a set deviates from the mean of the set by no more than the intra-laboratory precision statement. If, after several attempts, it is concluded that the ASTM procedures cannot be used for the specific coating with the established intra-laboratory precision (excluding UV radiation-cured coatings), the U.S. Environmental Protection Agency (EPA) will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emissions, Monitoring, and Analysis Division, MD-14, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

A = Area of substrate, cm², (in²).

C = Amount of coating or ink added to the substrate, g.

D_c = Density of coating or ink, g/cm³ (g/in³).

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F = Manufacturer's recommended film thickness, cm (in).

W_o = Weight fraction of nonaqueous volatile matter, g/g.

W_s = Weight fraction of solids, g/g.

W_v = Weight fraction of the volatile matter, g/g.

W_w = Weight fraction of the water, g/g.

12.2 To determine if a coating or ink can be classified as a thin-film UV cured coating or ink, use the following equation:

$$C = FAD_c \quad \text{Eq. 24-1}$$

12.3 Calculate W_v for each analysis as shown below:

$$W_v = \frac{W_1 - W_2}{W_3} \quad \text{Eq. 24-2}$$

12.4 Nonaqueous Volatile Matter.

12.4.1 Solvent-borne Coatings.

$$W_o = W_v \quad \text{Eq. 24-3}$$

12.4.2 Waterborne Coatings.

$$W_o = W_v - W_w \quad \text{Eq. 24-4}$$

12.4.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \quad \text{Eq. 24-5}$$

12.5 Weight Fraction Solids.

$$W_s = 1 - W_v \quad \text{Eq. 24-6}$$

12.6 Confidence Limit Calculations for Waterborne Coatings. To calculate the lower confidence limit, subtract the appropriate inter-laboratory precision value from the

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measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate inter-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits; for W_w, use the upper confidence limit. Because W_s is calculated, there is no adjustment for this parameter.

13.0 Method Performance

13.1 Analytical Precision Statements. The intra-and inter-laboratory precision statements are given in Table 24-1 in section 17.0.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as specified in section 6.0, with the addition of the following:

1. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA-340-1-91-010. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

2. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A.

EPA-340-1-91-011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

3. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumburg, IL. 1983.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 24-1—ANALYTICAL PRECISION STATEMENTS

	Intra-laboratory	Inter-laboratory
Volatile matter content, W _v	±0.015 W _v	±0.047 W _v
Water content, W _w	±0.029 W _w	±0.075 W _w
Density, D _c	±0.001 kg/l	±0.002 kg/l

METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PUBLICATION ROTOGRAVURE INKS AND RELATED PUBLICATION ROTOGRAVURE COATINGS

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Volatile organic compounds (VOC).	No CAS number assigned.

1.2 Applicability. This method is applicable for the determination of the VOC content and density of solvent-borne (solvent-reduc-

ible) publication rotogravure inks and related publication rotogravure coatings.

2.0 Summary of Method

2.1 Separate procedures are used to determine the VOC weight fraction and density of the ink or related coating and the density of the solvent in the ink or related coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the ink or related coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

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3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

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

5.2 Hazardous Components. Some of the compounds that may be contained in the inks or related coatings analyzed by this method may be irritating or corrosive to tissues or may be toxic. Nearly all are fire hazards. Appropriate precautions can be found in reference documents, such as Reference 6 of section 16.0.

6.0 Equipment and Supplies

The following equipment and supplies are required for sample analysis:

6.1 Weighing Dishes. Aluminum foil, 58 mm (2.3 in.) in diameter by 18 mm (0.7 in.) high, with a flat bottom. There must be at least three weighing dishes per sample.

6.2 Disposable Syringe. 5 ml.

6.3 Analytical Balance. To measure to within 0.1 mg.

6.4 Oven. Vacuum oven capable of maintaining a temperature of $120 \pm 2^\circ\text{C}$ ($248 \pm 4^\circ\text{F}$) and an absolute pressure of $510 \pm 51 \text{ mm Hg}$ ($20 \pm 2 \text{ in. Hg}$) for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of $120 \pm 2^\circ\text{C}$ ($248 \pm 4^\circ\text{F}$) for 24 hours.

6.5 The equipment and supplies specified in ASTM D 1475-60, 80, or 90 (incorporated by reference—see § 60.17).

7.0 Reagents and Standards

7.1 The reagents and standards specified in ASTM D 1475-60, 80, or 90 are required.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Follow the sample collection, preservation, storage, and transport procedures described in Reference 4 of section 16.0.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Additional guidance can be found in Reference 5 of section 16.0.

11.1 VOC Weight Fraction. Shake or mix the ink or related coating sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}). Using a 5 ml syringe, without a needle, extract an aliquot from the ink or related coating sample. Weigh the syringe and aliquot to the nearest 0.1 mg and record this weight (M_{cy1}). Transfer 1 to 3 g of the aliquot to the tared weighing dish. Reweigh the syringe and remaining aliquot to the nearest 0.1 mg and record this weight (M_{cy2}). Heat the weighing dish with the transferred aliquot in a vacuum oven at an absolute pressure of $510 \pm 51 \text{ mm Hg}$ ($20 \pm 2 \text{ in. Hg}$) and a temperature of $120 \pm 2^\circ\text{C}$ ($248 \pm 4^\circ\text{F}$) for 4 hours. Alternatively, heat the weighing dish with the transferred aliquot in a forced draft oven at a temperature of $120 \pm 2^\circ\text{C}$ for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure two times for each ink or related coating sample, for a total of three samples.

11.2 Ink or Related Coating Density. Determine the density of the ink or related coating (D_c) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the ink or related coating density as the arithmetic average (D_c) of the three determinations.

11.3 Solvent Density. Determine the density of the solvent (D_o) according to the procedure outlined in ASTM D 1475. Make a total of three determinations for each ink or related coating sample. Report the solvent density as the arithmetic average (D_o) of the three determinations.

12.0 Calculations and Data Analysis

12.1 VOC Weight Fraction. For each determination, calculate the volatile organic content weight fraction (W_o) using the following equation:

$$W_o = \frac{M_{x1} + M_{cy1} - M_{cy2} - M_{x2}}{M_{cy1} - M_{cy2}} \quad \text{Eq. 24A-1}$$

Make a total of three determinations. Report the VOC weight fraction as the arithmetic average (\bar{W}_o) of the three determinations.

12.2 VOC Volume Fraction. Calculate the volume fraction volatile organic content (V_o) using the following equation:

$$V_o = \frac{\overline{W}_o \overline{D}_c}{\overline{D}_o} \quad \text{Eq. 24A-2}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475.
2. Teleconversation. Wright, Chuck, Inmont Corporation with Reich, R., A., Radian Corporation. September 25, 1979, Gravure Ink Analysis.
3. Teleconversation. Oppenheimer, Robert, Gravure Research Institute with Burt, Rick, Radian Corporation, November 5, 1979, Gravure Ink Analysis.
4. Standard Procedure for Collection of Coating and Ink Samples for Analysis by Reference Methods 24 and 24A. EPA-340/1-91-010. U.S. Environmental Protection Agency,

Stationary Source Compliance Division, Washington, D.C. September 1991.

5. Standard Operating Procedure for Analysis of Coating and Ink Samples by Reference Methods 24 and 24A. EPA-340/1-91-011. U.S. Environmental Protection Agency, Stationary Source Compliance Division, Washington, D.C. September 1991.

6. Handbook of Hazardous Materials: Fire, Safety, Health. Alliance of American Insurers. Schaumberg, IL. 1983.

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

METHOD 25—DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total gaseous nonmethane organic compounds (TGNMO)	N/A	Dependent upon analytical equipment.

1.2 Applicability.

1.2.1 This method is applicable for the determination of volatile organic compounds (VOC) (measured as total gaseous nonmethane organics (TGNMO) and reported as carbon) in stationary source emissions. This method is not applicable for the determination of organic particulate matter.

1.2.2 This method is not the only method that applies to the measurement of VOC. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular composition of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

1.2.3 Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane (CH_4) will, of course, also be measured. The FID can be used under any of the

following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

1.2.4 Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

1.2.5 In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

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2.0 Summary of Method

2.1 An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to carbon dioxide (CO_2) and quantitatively collecting in the effluent in an evacuated vessel; then a portion of the CO_2 is reduced to CH_4 and measured by an FID. The organic content of the sample tank fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO_2 , and CH_4 ; the NMO are oxidized to CO_2 , reduced to CH_4 , and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Carbon Dioxide and Water Vapor. When carbon dioxide (CO_2) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent CO_2 and 10 percent water vapor, but it might be significant for a source having 10 percent CO_2 and 20 percent water vapor.

4.2 Particulate Matter. Collection of organic particulate matter in the condensate trap would produce a positive bias. A filter is included in the sampling equipment to minimize this bias.

5.0 Safety

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

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling system consists of a heated probe, heated filter, condensate trap, flow control system, and sample tank (see Figure 25-1). The TGNMO sampling equipment can be constructed from

commercially available components and components fabricated in a machine shop. The following equipment is required:

6.1.1 Heated Probe. 6.4-mm (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 °C (265 °F). The probe shall be equipped with a temperature sensor at the exit end to monitor the gas temperature. A suitable probe is shown in Figure 25-1. The nozzle is an elbow fitting attached to the front end of the probe while the temperature sensor is inserted in the side arm of a tee fitting attached to the rear of the probe. The probe is wrapped with a suitable length of high temperature heating tape, and then covered with two layers of glass cloth insulation and one layer of aluminum foil or an equivalent wrapping.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.2 Filter Holder. 25-mm (1 1/16-in.) ID Gelman filter holder with 303 stainless steel body and 316 stainless steel support screen with the Viton O-ring replaced by a Teflon O-ring.

6.1.3 Filter Heating System.

6.1.3.1 A metal box consisting of an inner and an outer shell separated by insulating material with a heating element in the inner shell capable of maintaining a gas temperature at the filter of 121 ± 3 °C (250 ± 5 °F). The heating box shall include temperature sensors to monitor the gas temperature immediately upstream and immediately downstream of the filter.

6.1.3.2 A suitable heating box is shown in Figure 25-2. The outer shell is a metal box that measures 102 mm × 280 mm × 292 mm (4 in. × 11 in. × 11 1/2 in.), while the inner shell is a metal box measuring 76 mm × 229 mm × 241 mm (3 in. × 9 in. × 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 ceramic fiber insulation which is sealed in place by means of a silicon rubber bead around the upper sides of the box. A removable lid made in a similar manner, with a 25-mm (1-in.) gap between the parts is used to cover the heating chamber. The inner box is heated with a 250-watt cartridge heater, shielded by a stainless steel shroud. The heater is regulated by a thermostatic temperature controller which is set to maintain a gas temperature of 121 °C (250 °F) as measured by the temperature sensor upstream of the filter.

NOTE: If it is not possible to use a heating system for safety reasons, an unheated system with an in-stack filter is a suitable alternative.

6.1.4 Condensate Trap. 9.5-mm (3/4-in.) OD 316 stainless steel tubing bent into a U-shape. Exact dimensions are shown in Figure

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25-3. The tubing shall be packed with coarse quartz wool, to a density of approximately 0.11 g/cm³ before bending. While the condensate trap is packed with dry ice in the Dewar, an ice bridge may form between the arms of the condensate trap making it difficult to remove the condensate trap. This problem can be prevented by attaching a steel plate between the arms of the condensate trap in the same plane as the arms to completely fill the intervening space.

6.1.5 Valve. Stainless steel control valve for starting and stopping sample flow.

6.1.6 Metering Valve. Stainless steel valve for regulating the sample flow rate through the sample train.

6.1.7 Rate Meter. Rotameter, or equivalent, capable of measuring sample flow in the range of 60 to 100 cm³/min (0.13 to 0.21 ft³/hr).

6.1.8 Sample Tank. Stainless steel or aluminum tank with a minimum volume of 4 liters (0.14 ft³).

NOTE: Sample volumes greater than 4 liters may be required for sources with low organic concentrations.

6.1.9 Mercury Manometer. U-tube manometer or absolute pressure gauge capable of measuring pressure to within 1 mm Hg in the range of 0 to 900 mm.

6.1.10 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

6.2 Condensate Recovery. The system for the recovery of the organics captured in the condensate trap consists of a heat source, an oxidation catalyst, a nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). Figure 25-4 is a schematic of a typical system. The system shall be capable of proper oxidation and recovery, as specified in section 10.1.1. The following major components are required:

6.2.1 Heat Source. Sufficient to heat the condensate trap (including probe) to a temperature of 200 °C (390 °F). A system using both a heat gun and an electric tube furnace is recommended.

6.2.2 Heat Tape. Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C (212 °F).

6.2.3 Oxidation Catalyst. A suitable length of 9.5 mm (3/8-in.) OD Inconel 600 tubing packed with 15 cm (6 in.) of 3.2 mm (3/8-in.) diameter 19 percent chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place.

6.2.4 Water Trap. Leak-proof, capable of removing moisture from the gas stream.

6.2.5 Syringe Port. A 6.4-mm (1/4-in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

6.2.6 NDIR Detector. Capable of indicating CO₂ concentration in the range of zero to 5 percent, to monitor the progress of combustion of the organic compounds from the condensate trap.

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6.2.7 Flow-Control Valve. Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

6.2.8 Intermediate Collection Vessel. Stainless steel or aluminum, equipped with a female quick connect. Tanks with nominal volumes of at least 6 liters (0.2 ft³) are recommended.

6.2.9 Mercury Manometer. Same as described in section 6.1.9.

6.2.10 Syringe. 10-ml gas-tight glass syringe equipped with an appropriate needle.

6.2.11 Syringes. 10-μl and 50-μl liquid injection syringes.

6.2.12 Liquid Sample Injection Unit. 316 Stainless steel U-tube fitted with an injection septum (see Figure 25-7).

6.3 Analysis.

6.3.1 NMO Analyzer. The NMO analyzer is a gas chromatograph (GC) with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. Figures 25-5 and 25-6 are schematics of a typical NMO analyzer. This semicontinuous GC/FID analyzer shall be capable of: (1) Separating CO, CO₂, and CH₄ from NMO, (2) reducing the CO₂ to CH₄ and quantifying as CH₄, and (3) oxidizing the NMO to CO₂, reducing the CO₂ to CH₄ and quantifying as CH₄, according to section 10.1.2. The analyzer consists of the following major components:

6.3.1.1 Oxidation Catalyst. A suitable length of 9.5-mm (3/8-in.) OD Inconel 600 tubing packed with 5.1 cm (2 in.) of 19 percent chromia on 3.2-mm (1/8-in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C (1200 °F) furnace. Longer catalysts mounted horizontally may be used, provided they can meet the specifications of section 10.1.2.1.

6.3.1.2 Reduction Catalyst. A 7.6-cm (3-in.) length of 6.4-mm (1/4-in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C (750 °F) furnace.

6.3.1.3 Separation Column(s). A 30-cm (1-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Unibeads 1S followed by a 61-cm (2-ft) length of 3.2-mm (1/8-in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve G. The Carbosieve and Unibeads columns must be baked separately at 200 °C (390 °F) with carrier gas flowing through them for 24 hours before initial use.

6.3.1.4 Sample Injection System. A single 10-port GC sample injection valve or a group of valves with sufficient ports fitted with a sample loop properly sized to interface with the NMO analyzer (1-cc loop recommended).

6.3.1.5 FID. An FID meeting the following specifications is required:

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6.3.1.5.1 Linearity. A linear response (± 5 percent) over the operating range as demonstrated by the procedures established in section 10.1.2.3.

6.3.1.5.2 Range. A full scale range of 10 to 50,000 ppm CH₄. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

6.3.1.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

6.3.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.3.3 Temperature Sensor. Capable of measuring the laboratory temperature within 1 °C (2 °F).

6.3.4 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

7.0 Reagents and Standards

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

7.1.1 Dry Ice. Solid CO₂, crushed.

7.1.2 Coarse Quartz Wool. 8 to 15 um.

7.1.3 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D2986-71, 78, or 95a (incorporated by reference—see §60.17). Test data from the supplier's quality control program are sufficient for this purpose.

7.2 NMO Analysis. The following gases are required for NMO analysis:

7.2.1 Carrier Gases. Helium (He) and oxygen (O₂) containing less than 1 ppm CO₂ and less than 0.1 ppm hydrocarbon.

7.2.2 Fuel Gas. Hydrogen (H₂), at least 99.99 percent pure.

7.2.3 Combustion Gas. Either air (less than 0.1 ppm total hydrocarbon content) or O₂ (purity 99.99 percent or greater), as required by the detector.

7.3 Condensate Analysis. The following are required for condensate analysis:

7.3.1 Gases. Containing less than 1 ppm carbon.

7.3.1.1 Air.

7.3.1.2 Oxygen.

7.3.2 Liquids. To conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society.

7.3.2.1 Hexane.

7.3.2.2 Decane.

7.4 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ± 5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum

shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required:

7.4.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

7.4.2 FID Linearity and NMO Calibration Gases. Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

7.4.3 CO₂ Calibration Gases. Three gas mixture standards with nominal CO₂ concentrations of 50 ppm, 500 ppm, and 1 percent, in air.

NOTE: Total NMO less than 1 ppm required for 1 percent mixture.

7.4.4 NMO Analyzer System Check Calibration Gases. Four calibration gases are needed as follows:

7.4.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH₄, 1 percent CO₂, and 20 ppm C₃H₈, prepared in air.

7.4.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

7.4.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

7.4.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling Equipment Preparation.

8.1.1 Condensate Trap Cleaning. Before its initial use and after each use, a condensate trap should be thoroughly cleaned and checked to ensure that it is not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in section 11.1.3. A trap may be considered clean when the CO₂ concentration in its effluent gas drops below 10 ppm. This check is optional for traps that most recently have been used to collect samples which were then recovered according to the procedure in section 11.1.3.

8.1.2 Sample Tank Evacuation and Leak-Check. Evacuate the sample tank to 10 mm Hg absolute pressure or less. Then close the sample tank valve, and allow the tank to sit for 60 minutes. The tank is acceptable if a change in tank vacuum of less than 1 mm Hg is noted. The evacuation and leak-check may be conducted either in the laboratory or the field.

8.1.3 Sampling Train Assembly. Just before assembly, measure the tank vacuum using a mercury manometer. Record this vacuum, the ambient temperature, and the barometric pressure at this time. Close the sample tank valve and assemble the sampling

system as shown in Figure 25-1. Immerse the condensate trap body in dry ice at least 30 minutes before commencing sampling to improve collection efficiency. The point where the inlet tube joins the trap body should be 2.5 to 5 cm (1 to 2 in.) above the top of the dry ice.

8.1.4 Pretest Leak-Check. A pretest leak-check is required. Calculate or measure the approximate volume of the sampling train from the probe tip to the sample tank valve. After assembling the sampling train, plug the probe tip, and make certain that the sample tank valve is closed. Turn on the vacuum pump, and evacuate the sampling system from the probe tip to the sample tank valve to an absolute pressure of 10 mm Hg or less. Close the purge valve, turn off the pump, wait a minimum period of 10 minutes, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 percent of the sampling rate using Equation 25-1, section 12.2. If the measured pressure change exceeds the allowable, correct the problem and repeat the leak-check before beginning sampling.

8.2 Sample Collection.

8.2.1 Unplug the probe tip, and place the probe into the stack such that the probe is perpendicular to the duct or stack axis; locate the probe tip at a single preselected point of average velocity facing away from the direction of gas flow. For stacks having a negative static pressure, seal the sample port sufficiently to prevent air in-leakage around the probe. Set the probe temperature controller to 129 °C (265 °F) and the filter temperature controller to 121 °C (250 °F). Allow the probe and filter to heat for about 30 minutes before purging the sample train.

8.2.2 Close the sample valve, open the purge valve, and start the vacuum pump. Set the flow rate between 60 and 100 cm³/min (0.13 and 0.21 ft³/hr), and purge the train with stack gas for at least 10 minutes.

8.2.3 When the temperatures at the exit ends of the probe and filter are within the corresponding specified ranges, check the dry ice level around the condensate trap, and add dry ice if necessary. Record the clock time. To begin sampling, close the purge

valve and stop the pump. Open the sample valve and the sample tank valve. Using the flow control valve, set the flow through the sample train to the proper rate. Adjust the flow rate as necessary to maintain a constant rate (± 10 percent) throughout the duration of the sampling period. Record the sample tank vacuum and flowmeter setting at 5-minute intervals. (See Figure 25-8.) Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulations; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained because of reduced sample tank vacuum.

NOTE: If sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After closing the sample tank valve, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train). Take another evacuated and leak-checked sample tank, measure and record the tank vacuum, and attach the new tank to the sampling train. After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

8.3 Sample Recovery. After sampling is completed, close the flow control valve, and record the final tank vacuum; then record the tank temperature and barometric pressure. Close the sample tank valve, and disconnect the sample tank from the sample system. Disconnect the condensate trap at the inlet to the rate meter, and tightly seal both ends of the condensate trap. Do not include the probe from the stack to the filter as part of the condensate sample.

8.4 Sample Storage and Transport. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that run numbers are identified on the condensate trap and the sample tank(s).

9.0 Quality Control

Section	Quality control measure	Effect
10.1.1	Initial performance check of condensate recovery apparatus.	Ensure acceptable condensate recovery efficiency.
10.1.2, 10.2	NMO analyzer initial and daily performance checks.	Ensure precision of analytical results.

10.0 Calibration and Standardization

NOTE: Maintain a record of performance of each item.

10.1 Initial Performance Checks.

10.1.1 Condensate Recovery Apparatus. Perform these tests before the system is first

placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the frequency recommended by the manufacturer.

10.1.1.1 Carrier Gas and Auxiliary O₂ Blank Check. Analyze each new tank of carrier gas or auxiliary O₂ with the NMO analyzer to