Method 25Aap -- Protocol for the Source Testing, Analysis, and Reporting of VOC Emissions from Hot Mix Asphalt Plant Dryers

Note: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling) essential to its performance. Some material has been incorporated from other methods in this part. Therefore, to obtain reliable results, those using this method should have a thorough knowledge of at least the following additional test methods: Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	< 2% of span

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons) referred to as Volatile Organic Compounds (VOC). This Protocol is recommended for the Source Testing, Analysis, and Reporting of VOC Emissions from Hot Mix Asphalt Plant Dryers (HMA). The mass emission rate of VOC from HMA plant dryers is expressed in terms of pounds per hour of propane.

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 **This protocol** is based on EPA's Reference Test Method 25A, as provided in 40 CFR Part 60 Appendix A, for the determination of total organic concentration. Specifically, the amended protocol provides for the avoidance of the moisture in the sampling and analysis of HMA stack emissions using flame ionization detection (FID) as identified in Method 25A. This amended protocol is then integrated into a comprehensive protocol, specifying Test Method 3C for speciation of methane and Test Method 316 for speciation of formaldehyde. This comprehensive protocol is to be used for source testing and quantifying proximate VOC emissions from HMA facility stacks. This comprehensive protocol also specifies appropriate calibration gas and molecular weight for purposes of quantifying and reporting emission results.

2.2 **Background.** The ability to accurately and easily measure organic emissions, e.g., VOCs in HMA dryer stack emissions, is of importance in meeting compliance obligations under the Clean Air Act. Historically, Test Method 25 or 25A has been the primary Reference Methods used for this purpose. However, Method 25 requires that the product of the percent CO_2 times the percent water in the flue gas be less than 100 in order for the measurements be valid. This product almost always is greater than 100. This leaves the measurement to Method 25A. However, moisture influence has been identified as potentially introducing negative bias caused by a reduction in the amount of oxygen reaching the flame in some analyzers. Moisture levels in gases from HMA dryer stacks are usually in the range of 20-30%.

In addition, flame ionization detection of short chain oxygenated compounds is also known to cause a low bias. In fact, the FID has no response to formaldehyde. Since formaldehyde is the primary oxygenated compound of interest in HMA dryer emissions, formaldehyde must be accurately quantified. Method 316 is least cumbersome and most practical method of the EPA reference methods for quantifying formaldehyde.

In addition, there is a need to accurately and easily quantify methane because methane is known to occur in significant quantities, relative to total organic emissions, in HMA dryer stack emissions. Because methane is non-photochemically reactive, and by EPA definition is not a VOC, it is appropriate to quantify methane using EPA Reference Test Method 3C. To accurately quantify VOC emissions, formaldehyde must be added to overall total organic emissions while methane must be subtracted from this value, to arrive at a reasonable and accurate estimate of VOC emissions in HMA plant dryer stacks.

3.0 Definitions [Reserved]

4.0 Interferences. [Reserved}

5.0 Safety

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

6.0 Equipment and Supplies.

See also Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

7.0 Reagents and Standards.

7.1.1 Calibration with propane in air. In order to have consistent reproducible results between sources Hot Mix Asphalt (HMA) plants, this protocol specifies only the selection to propane in air as calibration gases even though Method 25A allows several calibration gasses. Also the carrier gas and zero gas are specified as air, again for consistency. The following are additions to Method 25A:

7.1.2 The Zero Gas and dilution air shall be high purity air with less than a total VOC (FID response) of <0.1 ppm or <0.1% of the span value of the measurement system (which ever is less). The criteria for the zero gas shall be dry air that meets the zero gas described in 40 CFR 72.2.

7.1.3 The low-level calibration gas shall be EPA protocol propane in air with a concentration equivalent to 25 to 35 percent of the applicable span value of the measurement system.

7.1.4 The mid-level calibration gas shall be EPA protocol propane in air with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 The high-level calibration gas shall be EPA protocol propane in air with a concentration equivalent to 80 to 100 percent of the applicable span value of the measurement system.

7.1.6 Methane response factor calibration gas shall be EPA protocol methane in air with a concentration equivalent to about 25 percent of the applicable span value of the measurement system. Since propane has 3 times the number of carbons as methane (1), the methane concentration would be 3 times the propane concentration. See also Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

8.0 Sample Collection, Preservation, Storage, and Transport.

8.1 Method 25A additional specifications This comprehensive protocol relies on current analytical methodology as identified in U.S. EPA Reference Method 25A in 40 CFR Appendix A, amended to include a dilution technique, Alternate Test Method 007 (ALT-007), to reduce or eliminate the low bias caused by high moisture. This dilution protocol also has the advantage of decreasing the VOC/air ratio introduced into the FID. This reduced ratio usually

improves the consistency of the response factors and decreases the effect of moisture and carbon dioxide biases. This dilution protocol also specifies the analytical methodologies used in Method 3C for the determination of methane.

8.2 Dilution criteria with air for the elimination of moisture problems, ALT-007. Unlike the other instrumental reference methods, Method 25A determines VOC concentration on a wet basis. If the moisture content is high (over 10%) the flame is quenched and the FID reports a low biased VOC. One way to decrease the quenching effect of the FID flame is to dilute the stack gas below the quenching affect of the moisture. The dilution probe system has proven its reliability for use in EPA Methods 6C, 7E, 3A, 20, and 10.

The dilution probe system, however, usually requires an ambient concentration analyzer as well as the dilution probe. The FID instruments available today can easily measure VOC down to at least a range of 0 to 10 ppmw (part per million, wet). Using the Method 25A span criteria of 2.5 times the compliance level and a 20 to 1 dilution ratio, an 80 ppmw is the lowest compliance level that a span of 10 ppm should measure. Of course, if a more sensitive FID instrument were used, a lower compliance level could be obtained.

Although a dilution of 20 to 1 removes the potential of water condensation and flame quenching, it does not remove the potential of condensing the VOC. Thus, the sample line and filter must be maintained at ≥121°C (250°F) or the stack temperature which ever is greater. When the stack temperature is less than 121°C (250°F) the filter temperature should still be maintained ≥121°C (250 °F). However, the sample line should not exceed 177 (350°F) to keep the line form melting. In addition to meeting all the criteria in Method 25A, the following are additions to Method 25A:

8.3 The measurement system as, defined in this method, includes a heated dilution probe (in or out of the stack), heated filter, heated sample line and an FID instrument. All calibrations shall include the dilution probe, filter, heated sample line and heated FID instrument.

8.4 The dilution probe of Test shall have a dilution ratio of at least a 10 to 1; however, a dilution ratio of 20 to 1 or more is recommended. The heated dilution system is shall immediately follow the probe and filter if it is not in the stack. It shall dilute with dry air that has total VOC less than 0.1 ppm. The amount of dilution will depend upon the compliance level.

Example 1: If the compliance level is 100 ppmw as propane and the FID instrument span is 10 ppmw as propane, the span of the measurement system must be between 150 and 250 ppmw in order to meet Method 25A criteria of 1.5 to 2.5 times the compliance level. If the span is set at 200 before dilution, then the dilution ratio is 200/10 or 20/1 and compliance level is a reading of 5 ppmw on the FID. The dilution value must be multiplied times the FID instrument reading to obtain the correct answer as ppmw propane. With a zero and dilution gas with a VOC concentration of less than 0.1 ppm, the imprecision due to the dilution gas at compliance level would then be less than ±0.1 of the instrument span of 10 or ± 2.0 ppmw at a compliance level of 100.

8.5 The location of the probe entrance shall be so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

8.6 The FID instrument shall be adjusted to a nominal span of about 10 ppmw (part per million, wet). The sample line and filter shall be maintained at ≥ 121°C (250°F) or the stack temperature which ever is greater. The sample line from the dilution probe to the FID must be maintained at ≥121°C (250°F) to prevent the VOCs from condensing. However, the sample line should not exceed 177 (350°F). The whole system shall be heated and insolated (not just insolated) included connectors.

8.8 Use Method 3C. for Methane determination Since methane is not a VOC, it is highly recommended that it should be measured by Method 3C and then subtracted from the Method 25A measurement. The following are recommended additions to Method 25A:

8.8 **Collect the methane sample** for each run directly from the middle of the stack into a canister or bag using Method 3. Since methane is non-reactive, does not dissolve in water and has a very high vapor pressure it can be collected in a canister instead of a bag if desired. The moisture may be condensed in the bag or in a chilled midget impinger before the bag. Condensing in chilled midget impinger is preferred. Since the water is condensed, the methane analysis is on the dry basis.

8.9 Use Methods 1 through 4 for the determination of Q_{sd} (flue gas flow rate in dry standard cubic feet per minute).

8.9.1 Use Method 1 to select the number of velocity traverse points and to determine the absence of cyclonic flow.

8.9.2 Use Method 2 to determine the flue gas flow rate.

8.9.3 Use Method 3 for determining the flue gas dry molecular weight or use an Alternative to Method 3. It is recommended that the dry molecular weight be assigned a value of 29.4. This value reflects a 5% CO_2 content which is typical for HMA plants burning oil or natural gas. Method 3 allows the "assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil". The use of 30 instead of 29.4 will cause a 1% high bias of the PMR_{VOC}. Therefore, it is recommended that a value of 29.4 be assigned for the molecular weight.

8.9.4 Use Method 4 to determine the moisture. If methane and formaldehyde are not to be measured, then moisture becomes less important. (Usually methane and formaldehyde are small as compared to the VOC.) This is because moisture is then only needed to calculate the stack gas molecular weight and PMR_{VOC} can be calculated using the wet stack gas flowrate. (The effect on the molecular weight PMR_{VOC} is small or ±2% for moistures of 15% to 35%). This being the case, moisture can be determined using the approximation method or other alternative means, such as wet bulb-dry bulb techniques or even estimation, when methane and formaldehyde are not to be measured.

8.10 Formaldehyde determination if needed by EPA Method 316. See also Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

9.0 Quality Control.

See Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

10.0 Calibration and Standardization.

10.1 For calibration, the zero gas and three calibration gases must always be introduced at the tip of the probe and travel through the entire system. Calibration error, response time and drift determinations should be done according to Method 25A except the calibrations gasses should always travel through the entire system

10.2 Calibration with propane in air. In order to have consistent reproducible results between sources Hot Mix Asphalt (HMA) plants, this protocol specifies only the selection to propane even though Method 25A allows several calibration gasses. Also the carrier gas and zero gas are specified as air, again for consistency

10.3 Calibration the FID for a methane response. The response factor per carbon in a FID is usually higher for methane (usually by about 5% to 20%) than that of propane per carbon, so a

response factor for methane needs to be determined. To fix this problem, calibrate the system with methane also.

11.0 Analytical Procedures.

Measure the Methane concentration using Method 3C for analysis except substitute a FID detector in place of a TCD.

See also Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

12.0 Calculations and Data Analysis.

12.1 Establishing a response factor for methane is accomplished by challenging the whole measurement system on site before the test with about 25% span concentration of protocol methane. Since propane has 3 times the number of carbons as methane (1), the methane concentration would be 3 times the propane concentration.

Example 2: Using example 1 from above, a measurement system span of 200 ppmw as propane would require 150 ppm methane and should give about a 60 ppm as propane response. The response factor would be 3 times 60 divided by 150 (or 1.20). If a Method 3C run yields a methane value of 45 ppm, then 1.2 times 45 divided by 3 (or 18) should be subtracted from run 1 measurement system average value.

The equations 25Aap-1 is as follows.

$$RF = \frac{3 * C_p}{C_m}$$

Where:

RF = response factor

C_m = methane concentration from calibrated methane tank.

C_{mp} = response from measurement system as propane when injecting C_m

12.2 The Methane concentration should be subtracted from each run average VOC concentration from the measurement system after multiplying the methane concentration by the response factor and divided by 3 and the M_{fd} described in equation 25Aap - 2.

$$\overline{ppm_w} = \frac{\sum ppm_i}{n_i} - \frac{RF * C_{mr1} * M_{fd}}{3}$$

Where

C_{mr1} =methane concentration from the Method 3C run 1 analysis, ppmd.

n_i =number of individual readings.

ppm_i= individual VOC response from measurement system as propane

= average concentration of VOC less methane.

M_{fd} = mole fraction of dry gas

$\overline{ppm_w}$ **Example 3:** If a Method 3C run from a 30% moisture stack the M_{fd} = 1-30% moisture/100 = 0.7. If the Method 3C analysis yields a methane value of 45 ppm, then 1.2 times 45 times 0.7 divided by 3 (= 12.6) should be subtracted from run 1 measurement system average value.

12.3 Conversion of the VOC concentration to mass emission. A short coming of both Method 25 and 25A has been the lack of a molecular weight for determining the mass of VOC per hour. Most all state regulations require a pound per hour emission rate determination of a sources VOC. The methods do not determine molecular weight or molecular weight per carbon (MW/C). Because of this, testers have used the molecular weight of carbon (12), methane (16 per carbon) and propane (44/3 or 14.67 per carbon). EPA emission factors for HMA plants in AP-42 when excluding formaldehyde and methane uses a MW/C of 12.9 when heating with natural gas, 14.2 when heating with #2 fuel oil and 15.9 when heating with waste oil. This is about ±10% of the MW/C for propane or 14.67. This protocol recommends (for consistency) that the molecular weight of propane be used for the determination of the mass emission rate of VOC from the VOC concentration measured as propane. The following recommendations are additions to Method 25A:

12.4 To determine pounds per hour VOC, use the following equation 25Aap-3.

$$PMR_{VOC} = \frac{60 \times \overline{ppm}_w \times F_{wt} \times Q_{sd}}{385.3 \times 10^6 \times M_{fd}}$$

PMR_{VOC} = pounds per hour VOC.

ppm_w = parts per million by volume wet of VOC (or VOC less methane).

M_{fd} = mole fraction of dry gas

F_{wt} = formula weight for propane (recommended) is 44.10.

Q_{sd} = flue gas flow rate in dry standard cubic feet per minute.

12.5 Total formaldehyde pollutant mass rate PMR_{FOR} is calculated from the formaldehyde concentration (expressed as mg/m^3) from Method 316 using the following equation 25Aap-4:

$$PMR_{FOR} = \frac{3.746 \times C_{FOR} \times Q_{sd}}{10^6}$$

Where:

C_{FOR} = concentration of formaldehyde, mg/M^3

PMR_{FOR} = pounds per hour formaldehyde.

12.6 The pollutant mass rate of VOC emissions would then be the sum of the PMR_{VOC} plus the PMR_{FOR} as in equation 25Aap-5.

$$PMR_{TOT} = PMR_{VOC} + PMR_{FOR}$$

Where:

PMR_{TOT} =Total pounds per hour VOC.

13.0 Method Performance.

See Methods 1, 2, 3 or 3C, 4, 25A, 316, and ALT 007.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

U.S. EPA (1995). *Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition, Volume I: Stationary Point and Area Sources, Introduction*. United States Environmental Protection Agency, Technology Transfer Network, Clearinghouse for Inventories & Emission Factors, January 1995, Available at: http://www.epa.gov/ttn/chief/ap42/c00s00.pdf.

U.S. EPA (2004a). *Emission Factor Documentation for AP-42 Section 11.1 Hot Mix Asphalt Plants Final Report*. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Measurement Center, February 2004, Available at: http://www.epa.gov/ttn/chief/ap42/ch11/bgdocs/b11s01.pdf

U.S. EPA (2004b). *Compilation of Air Pollutant Emission Factors, AP-42, Fifth Edition Chapter 11.1: Hot Mix Asphalt Plants*. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Measurement Center, February 2004, Available at: http://www.epa.gov/ttn/chief/ap42/ch11/final/c11s01.pdf

17.0 Tables, Diagrams, Flowcharts, and Validation Data.

ALT-007 TEST METHODS 6C, 7E, 3A, 20, AND 10 USE OF DILUTION PROBES WITH INSTRUMENTAL METHODS

INTRODUCTION

The Environmental Protection Agency (EPA) Methods 6C, 7E, 3A, 20, and 10 provide specifications for testing pollutants in stationary source exhausts with instrumental measurement systems. The methods call for the determination of a pollutant concentration on a dry basis. However, increased monitoring of exhaust gas emission standards on a pounds per hour (lbs/hr) basis, has resulted in the use of instrumental reference methods which evaluate concentrations on a wet basis. The dilution probe system has proven its reliability for use in the above EPA methods.

The dilution probe system is usually comprised of an ambient concentration analyzer and the dilution probe. Since this system dilutes high moisture stack gas, heating the sample is generally not necessary. Another advantage to non-dilution systems is that lower sample volumes are required. In comparison, non-dilution systems employ sample conditioning systems which physically remove moisture and are usually designed to obtain a dry concentration value.

GUIDELINE

Instrumental system dilution ratios range from 12:1 to 350:1; therefore, certain clarifications are necessary for the use of the dilution probe system:

Span: Method 6C defines span as "the upper limit of the gas concentration measurement range displayed on the data recorder." The dilution monitoring system should report concentrations that have been corrected for the dilution ratio. Therefore, the data recorder should be capable of displaying the ambient analyzer response, the amount of dilution, and combine the two for the higher range concentrations corrected for dilution. The actual span of the analyzer should be set such that this "regulatory" span or upper recorder limit is achieved. For example, if a "regulatory" span was set at 300 ppm and the dilution ratio was 10:1 then the actual span for the analyzer would be set at 30 ppm and the signal amplified or multiplied by 10 before being displayed.

Calibration Gases: The required zero, mid and high-level calibration gas values are also based on the specified span values. The dilution ratio shall be recorded after the system has been set up using an appropriate Protocol 1 gas (Method 6C, Section 6.3.1).

Calibration: The introduction of the three calibration gases must be prior to the glass orifice or at the probe tip. The bias check of Section 6.4.2 is still ±5 percent based on the established span value.

Wet Basis Calculations: Concentrations are reported on a wet basis. Therefore, a separate water determination may be necessary to correct to dry gas concentrations. If the dilution monitoring system is used to test a continuous emission monitoring system the data from both systems must be on a comparative basis (i.e., all data on a wet basis).

In conclusion, dilution probes are acceptable and must be included as part of the measurement system when conducting the applicable performance specification test.

Method 3C – Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources1. Applicability and Principle

1.1 Applicability. This method applies to the analysis of carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), and oxygen (O_2) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart.

1.2 Principle. A portion of the sample is injected into a gas chromatograph (GC) and the CO_2, CH_4, N_2, and O_2 concentrations are determined by using a thermal conductivity detector (TCD) and integrator.

2. Range and Sensitivity

2.1 Range. The range of this method depends upon the concentration of samples. The analytical range of TCD's is generally between approximately 10 ppmv and the upper percent range.

2.2 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. For CO_2, CH_4, N_2, and O_2, the sensitivity limit is in the low ppmv range.

3. Interferences

Since the TCD exhibits universal response and detects all gas components except the carrier, interferences may occur. Choosing the appropriate GC or shifting the retention times by changing the column flow rate may help to eliminate resolution interferences.

To assure consistent detector response, helium is used to prepare calibration gases. Frequent exposure to samples or carrier gas containing oxygen may gradually destroy filaments.

Temp., oC	Vapor Pressure of H_2O, mm Hg	Temp., oC	Vapor Pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

Table 3C-1. MOISTURE CORRECTION

4. Apparatus

4.1 Gas Chromatograph. GC having at least the following components:

4.1.1 Separation Column. Appropriate column(s) to resolve CO_2, CH_4, N_2, O_2, and other gas components that may be present in the sample.

4.1.2 Sample Loop. Teflon or stainless steel tubing of the appropriate diameter. Note: Mention of trade names or specific products does not constitute endorsement or recommendation by the U. S. Environmental Protection Agency.

4.1.3 Conditioning System. To maintain the column and sample loop at constant temperature.

4.1.4 Thermal Conductivity Detector.

4.2 Recorder. Recorder with linear strip chart. Electronic integrator (optional) is recommended.

4.3 Teflon Tubing. Diameter and length determined by connection requirements of cylinder regulators and the GC.

4.4 Regulators. To control gas cylinder pressures and flow rates.

4.5 Adsorption Tubes. Applicable traps to remove any O_2 from the carrier gas.

5. Reagents

5.1 Calibration and Linearity Gases. Standard cylinder gas mixtures for each compound of interest with at least three concentration levels spanning the range of suspected sample concentrations. The calibration gases shall be prepared in helium.

5.2 Carrier Gas. Helium, high-purity.

6. Analysis

6.1 Sample Collection. Use the sample collection procedures described in Methods 3 or 25C to collect a sample of landfill gas (LFG).

6.2 Preparation of GC. Before putting the GC analyzer into routine operation, optimize the operational conditions according to the manufacturer's specifications to provide good resolution and minimum analysis time. Establish the appropriate carrier gas flow and set the detector sample and reference cell flow rates at exactly the same levels. Adjust the column and detector temperatures to the recommended levels. Allow sufficient time for temperature stabilization. This may typically require 1 hour for each change in temperature.

6.3 Analyzer Linearity Check and Calibration. Perform this test before sample analysis. Using the gas mixtures in section 5.1, verify the detector linearity over the range of suspected sample concentrations with at least three points per compound of interest. This initial check may also serve as the initial instrument calibration. All subsequent calibrations may be performed using a single-point standard gas provided the calibration point is within 20 percent of the sample component concentration. For each instrument calibration, record the carrier and detector flow rates, detector filament and block temperatures, attenuation factor, injection time, chart speed, sample loop volume, and component concentrations. Plot a linear regression of the standard concentrations versus area values to obtain the response factor of each compound. Alternatively, response factors of uncorrected component concentrations (wet basis) may be generated using instrumental integration. Note: Peak height may be used instead of peak area throughout this method.

6.4 Sample Analysis. Purge the sample loop with sample, and allow to come to atmospheric pressure before each injection. Analyze each sample in duplicate, and calculate the average sample area (A). The results are acceptable when the peak areas for two consecutive injections agree within 5 percent of their average. If they do not agree, run additional samples until consistent area data are obtained. Determine the tank sample concentrations according to section 7.2.

7. Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

7.1 Nomenclature.

A = average sample area

Bw = moisture content in the sample, fraction

C = component concentration in the sample, dry basis, ppmv

Ct = calculated NMOC concentration, ppmv C equivalent

Ctm = measured NMOC concentration, ppmv C equivalent

Pbar = barometric pressure, mm Hg

Pti = gas sample tank pressure after evacuation, mm Hg absolute

Pt = gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute

Ptf = final gas sample tank pressure after pressurizing, mm Hg absolute

Pw = vapor pressure of H_2O (from table 3C-1), mm Hg

Tti = sample tank temperature before sampling, °K

Tt = sample tank temperature at completion of sampling, °K

Ttf = sample tank temperature after pressurizing, °K

r = total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r)

R = Mean calibration response factor for specific sample component, area/ppmv

7.2 Concentration of Sample Components. Calculate C for each compound using Equations 3C-1 and 3C-2. Use the temperature and barometric pressure at the sampling site to calculate B_w. If the sample was diluted with helium using the procedures in Method 25C, use Equation 3C-3 to calculate the concentration.

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1-B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1-B_w)} \qquad 3C\text{-}3$$

Method 25A -- Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Total Organic Compounds	N/A	< 2% of span

1.2 Applicability. This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

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

2.0 Summary of Method

2.1 A gas sample is extracted from the source through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

3.0 Definitions

3.1 *Calibration drift* means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.2 *Calibration error* means the difference between the gas concentration indicated by the measurement system

and the know concentration of the calibration gas.

3.3 *Calibration gas* means a known concentration of a gas in an appropriate diluent gas.

3.4 *Measurement system* means the total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 *Sample interface* means that portion of a system used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 *Organic analyzer* means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 *Response time* means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 *Span Value* means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 *Zero drift* means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

5.2 Explosive Atmosphere. This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

6.0 Equipment and Supplies

6.1 Measurement System. Any measurement system for total organic concentration that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 25A-1. All sampling components leading to the analyzer shall be heated ≥ 110 °C (220 °F) throughout the sampling period, unless safety reasons are cited (Section 5.2) The essential components of the measurement system are described below:

6.1.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications of this method. The flame ionization detector block shall be heated >120 °C (250 °F).

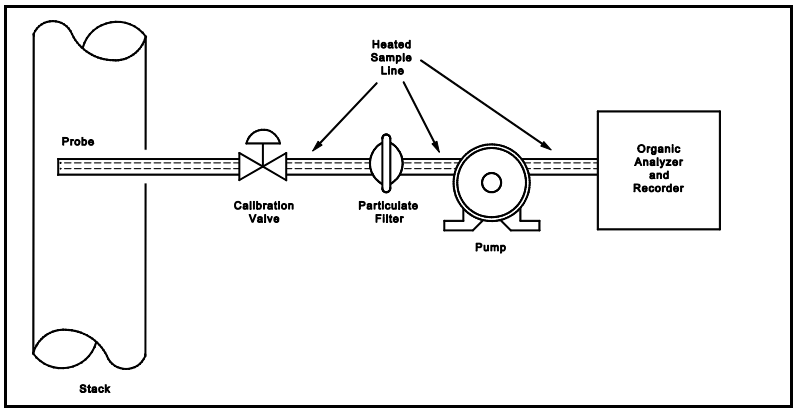


Figure 25A-1 Organic Concentration Measurement System.

6.1.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm (0.16-in.) in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

6.1.3 Heated Sample Line. Stainless steel or Teflon" tubing to transport the sample gas to the analyzer. The sample line should be heated (≥110 °C) to prevent any condensation.

6.1.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

6.1.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

6.1.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute.

7.0 Reagents and Standards

7.1 Calibration Gases. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. Alternatively, organic compounds other than propane can be used; the appropriate corrections for response factor must be made. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of Section 16. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ± 2 percent from the certified value. For calibration gas values not generally available (*i.e.,* organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.1.1 Fuel. A 40 percent H2/60 percent N2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.1.2 Zero Gas. High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.1.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.1.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.1.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test (*i.e.,* exhaust stack, inlet line, etc.). The sample port shall be located to meet the testing requirements of Method 1.

8.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

8.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system by following the manufacturer's written instructions for preparing sample interface and the organic analyzer. Make the system operable (Section 10.1).

8.4 Calibration Error Test. Immediately prior to the test series (within 2 hours of the start of the test), introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level response. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 8.6.2). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

8.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

8.6 Emission Measurement Test Procedure.

8.6.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particulate, note on the recording chart, periods of process interruption or cyclic operation.

8.6.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 8.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

Note: Note on the recording chart periods of process interruption or cyclic operation.

9.0 Quality Control

Method	Quality Control Measure	Effect
8.4	Zero and calibration drift tests.	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 3 percent of span.

10.0 Calibration and Standardization

10.1 FIA equipment can be calibrated for almost any range of total organic concentrations. For high concentrations of organics (> 1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Analytical Procedure

The sample collection and analysis are concurrent for this method (see Section 8.0).

12.0 Calculations and Data Analysis

12.1 Determine the average organic concentration in terms of ppmv as propane or other calibration gas. The average shall be determined by integration of the output recording over the period specified in the applicable regulation. If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_{meas} \qquad Eq.\ 25A\text{-}1$$

Where:

Cc = Organic concentration as carbon, ppmv.

Cmeas = Organic concentration as measured, ppmv.

K = Carbon equivalent correction factor.
= 2 for ethane.
= 3 for propane.
= 4 for butane.
= Appropriate response factor for other organic calibration gases.

13.0 Method Performance

13.1 Measurement System Performance Specifications.

13.1.1 Zero Drift. Less than ±3 percent of the span value.

13.1.2 Calibration Drift. Less than ±3 percent of span value.

13.1.3 Calibration Error. Less than ±5 percent of the calibration gas value.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Measurement of Volatile Organic Compounds -- Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

2. EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. U.S. Environmental Protection Agency, Quality Assurance and Technical Support Division. Research Triangle Park, N.C. September 1993.

3. Gasoline Vapor Emission Laboratory Evaluation -- Part 2. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Trian-

gle Park, NC. EMB Report No. 75-GAS-6. August 1975.

17.0 Tables, Diagrams, Flowcharts, and Validation Data.

Method 316 - Sampling and Analysis for Formaldehyde Emissions from Stationary Sources in the Mineral Wool and Wool Fiberglass Industries

1.0 Introduction.

This method is applicable to the determination of formaldehyde, CAS Registry number 50-00-0, from stationary sources in the mineral wool and wool fiber glass industries. High purity water is used to collect the formaldehyde. The formaldehyde concentrations in the stack samples are determined using the modified pararosaniline method. Formaldehyde can be detected as low as 8.8 x 10^{-10} lbs/cu ft (11.3 ppbv) or as high as 1.8 x 10^{-3} lbs/cu ft (23,000,000 ppbv), at standard conditions over a 1 hour sampling period, sampling approximately 30 cu ft.

2.0 Summary of Method.

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in high purity water. Formaldehyde present in the emissions is highly soluble in high purity water. The high purity water containing formaldehyde is then analyzed using the modified pararosaniline method. Formaldehyde in the sample reacts with acidic pararosaniline, and the sodium sulfite, forming a purple chromophore. The intensity of the purple color, measured spectrophotometrically, provides an accurate and precise measure of the formaldehyde concentration in the sample.

3.0 Definitions.

See the definitions in the General Provisions of this Subpart.

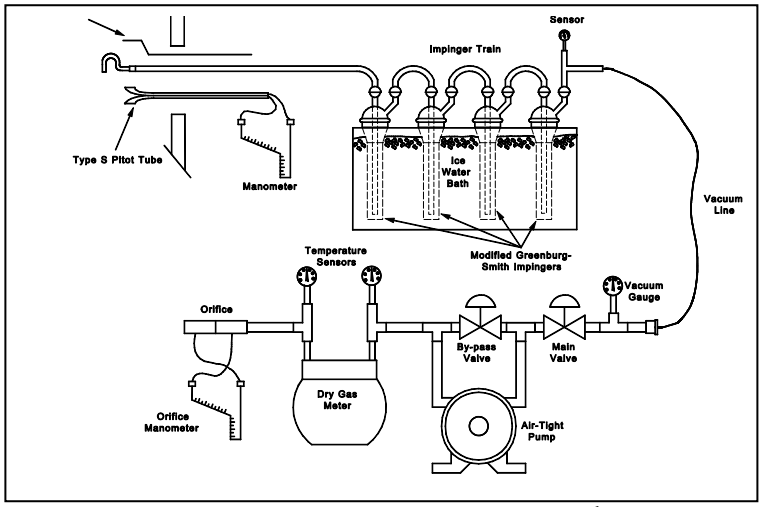
4.0 Interferences.

Sulfite and cyanide in solution interfere with the pararosaniline method. A procedure to overcome the interference by each compound has been described by Miksch, et al.

5.0 Safety. (Reserved)

6.0 Apparatus and Materials.

6.1 A schematic of the sampling train is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5, 40 CFR part 60, appendix A, procedures. The sampling train consists of the following components: probe nozzle, probe liner, Pitot tube, differential pressure gauge, impingers, metering system, barometer, and gas density determination equipment.



6.1.1 Probe Nozzle: Quartz, glass, or stainless steel with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.15 cm (1/16 in), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedure outlined in Section 10.1.

6.1.2 Probe Liner: Borosilicate glass or quartz shall be used for the probe liner. The probe shall be maintained at a temperature of 120°C ± 14°C (248°F ± 25°F).

6.1.3 Pitot Tube: The Pitot tube shall be Type S, as described in Section 2.1 of EPA Method 2, 40 CFR part 60, appendix A, or any other appropriate device. The Pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the Pitot tube shall be even with or above the nozzle entry plane (see Figure 2-6b, EPA Method 2, 40 CFR part 60, appendix A) during sampling. The Type S Pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2, 40 CFR part 60, appendix A.

6.1.4 Differential Pressure Gauge: The differential pressure gauge shall be an inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2, 40 CFR part 60, appendix A. One manometer shall be used for velocity-head reading and the other for orifice differential pressure readings.

6.1.5 Impingers: The sampling train requires a minimum of four impingers, connected as shown in Figure 1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameters (1/2 in) glass tube extending to 1.3 cm (1/2 in) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Place a thermometer capable of measuring temperature to within 1°C (2°F) at the outlet of the fourth impinger for monitoring purposes.

6.1.6 Metering System: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperatures within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1 percent, and related equipment as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems may be used which are capable of maintaining sample volumes to within 2 percent. The metering system may be used in conjunction with a Pitot tube to enable checks of isokinetic sampling rates.

6.1.7 Barometer: The barometer may be mercury, aneroid, or other barometer capable of measuring atmospheric pres-

sure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase (rate is plus 2.5 mm Hg per 30 m (100 ft) of elevation decrease).

6.1.8 Gas Density Determination Equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.3 of EPA Method 2, 40 CFR part 60, appendix A), and gas analyzer, if necessary (as described in EPA Method 3, 40 CFR part 60, appendix A). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the top of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S Pitot openings (see Figure 2-7, EPA Method 2, 40 CFR part 60, appendix A). As a second alternative, if a difference of no more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or Pitot tube.

6.2 Sample Recovery.

6.2.1 Probe Liner: Probe nozzle and brushes; bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon™, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.

6.2.2 Wash Bottles: One wash bottle is required. Polyethylene, Teflon™, or glass wash bottles may be used for sample recovery.

6.2.3 Graduated Cylinder and/or Balance: A graduated cylinder or balance is required to measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have division not > 2 ml. Laboratory balances capable of weighing to ± 0.5 g are required.

6.2.4 Polyethylene Storage Containers: 500 ml wide-mouth polyethylene bottles are required to store impinger water samples.

6.2.5 Rubber Policeman and Funnel: A rubber policeman and funnel are required to aid the transfer of material into and out of containers in the field.

6.3 Sample Analysis.

6.3.1 Spectrophotometer - B&L 70, 710, 2000, etc., or equivalent; 1 cm pathlength cuvette holder.

6.3.2 Disposable polystyrene cuvettes, pathlengh 1 cm, volume of about 4.5 ml.

6.3.3 Pipettors - Fixed-volume Oxford pipet (250 µl; 500 µl; 1000 µl); adjustable volume Oxford or equivalent pipettor 1-5 ml model, set to 2.50 ml.

6.3.4 Pipet tips for pipettors above.

6.3.5 Parafilm, 2° wide; cut into about 1" squares.

7.0 Reagents.

7.1 High purity water: All references to water in this method refer to high purity water (ASTM Type I water or equivalent). The water purity will dictate the lower limits of formaldehyde quantification.

7.2 Silica Gel: Silica gel shall be indicting type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

7.3 Crushed Ice: Quantities ranging from 10-50 lbs may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient ice for this purpose must be allowed.

7.4 Quaternary ammonium compound stock solution: Prepare a stock solution of dodecyltrimethylammonium chloride (98 percent minimum assay, reagent grade) by dissolving 1.0 gram in 1000 ml water. This solution contains nominally 1000 µg/ml quaternary ammonium compound, and is used as a biocide for some sources which are prone to microbial contamination.

7.5 Pararosaniline: Weigh 0.16 grams pararosaniline (free base; assay of 95 percent or greater, C.I. 42500; Sigma P7632 has been found to be acceptable) into a 100 ml flask. Exercise care, since pararosaniline is a dye and will stain. Using a wash bottle with high-purity water, rinse the walls of the flask. Add no more than 25 ml water. Then, carefully add 20 ml of concentrated hydrochloric acid to the flask. The flask will become warm after the addition of acid. Add a magnetic stir bar to the flask, cap, and place on a magnetic stirrer for approximately 4 hours. Then, add additional water so the total volume is 100 ml. This solution is stable for several months when stored tightly capped at room temperature.

7.6 Sodium sulfite: Weigh 0.10 grams anhydrous sodium sulfite into a 100 ml flask. Dilute to the mark with high purity water. Invert 15-20 times to mix and dissolve the sodium sulfite. This solution MUST BE PREPARED FRESH EVERY DAY.

7.7 Formaldehyde standard solution: Pipet exactly 2.70 ml of 37 percent formaldehyde solution into a 1000 ml volumetric flask which contains about 500 ml of high-purity water. Dilute to the mark with high-purity water. This solution contains nominally 1000 µg/ml of formaldehyde, and is used to prepare the working formaldehyde standards. The exact formaldehyde concentration may be determined if needed by suitable modification of the sodium sulfite method (Reference: J.F. Walker, FORMALDEHYDE (Third Edition), 1964.). The 1000 µg/ml formaldehyde stock solution is stable for at least a year if kept tightly closed, with the neck of the flask sealed with Parafilm. Store at room temperature.

7.8 Working formaldehyde standards: Pipet exactly 10.0 ml of the 1000 µg/ml formaldehyde stock solution into a 100 ml volumetric flask which is about half full of high-purity water. Dilute to the mark with high-purity water, and invert 15-20 times to mix thoroughly. This solution contains nominally 100 µg/ml formaldehyde. Prepare the working standards from this 100 µg/ml standard solution and using the Oxford pipets:

Working Standard, µ/mL	**µL or 100 µg/mL Solution**	**Volumetric Flask Volume (Dilute to mark with water)**
0.250	250	100
0.500	500	100
1.00	1000	100
2.00	2000	100
3.00	1500	50

The 100 µg/ml stock solution is stable for 4 weeks if kept refrigerated between analyses. The working standards (0.25 - 3.00 µg/ml) should be prepared fresh every day, consistent with good laboratory practice for trace analysis. If the laboratory water is not of sufficient purity, it may be necessary to prepare the working standards EVERY DAY. The

laboratory MUST ESTABLISH that the working standards are stable - DO NOT assume that your working standards are stable for more than a day unless you have verified this by actual testing for several series of working standards.

8.0 Sample Collection.

8.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

8.2 Laboratory Preparation:

Plant.....
Location.....
Operator.....
Date .....
Run No .....
Sample box No .....
Meter box No.....
Meter ΔH.....
C Factor.....
Pitot tube coefficient, Cp .....

SCHEMATIC OF STACK CROSS SECTION

Ambient temperature……
Barometric pressure……
Assumed moisture, percent……
Probe length, m (ft)……
Nozzle Identification No……
Average calibrated nozzle diameter, cm (in.)……
Probe heater setting……
Leak rate, m^3/min (cfm)……
Probe liner material……
Static pressure, mm Hg (in. Hg)……
Filter No……

Traverse point number	Sampling time (e) min.	Vacuum mm Hg (in. Hg)	Stack temperature (T) °C (°F)	Velocity head (ΔP) mm (in) H_2O	Pressure differential across orifice meter mm H_2O (in. H_2O)	Gas sample volume m^3 (ft^3)	Gas sample temperature at dry gas meter		Filter holder temperature °C (°F)	Temperature of gas leaving condenser or last impinger °C (°F)
							Inlet °C (°F)	Outlet °C (°F)		
Total							Avg.	Avg.		
Average							Avg.			

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

8.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

8.3 Preliminary Field Determinations.

8.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1, 40 CFR part 60, appendix A, or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2, 40 CFR part 60, appendix A. A leak-check of the Pitot lines according to Section 3.1 of EPA Method 2, 40 CFR part 60, appendix A, must be performed. Determine the stack gas moisture content using EPA Approximation Method 4,40 CFR part 60, appendix A, or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, 40 CFR part 60, appendix A, Section 3.6. If integrated EPA Method 3, 40 CFR part 60, appendix A, sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 l/min (1.0 cfm). During the run do not change the nozzle. Ensure that the proper differential pressure

gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2, 40 CFR part 60, appendix A).

8.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

8.3.4 A minimum of 30 cu ft of sample volume is suggested for emission sources with stack concentrations not greater than 23,000,000 ppbv. Additional sample volume shall be collected as necessitated by the capacity of the water reagent and analytical detection limit constraint. Reduced sample volume may be collected as long as the final concentration of formaldehyde in the stack sample is greater than 10 (ten) times the detection limit.

8.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1, 40 CFR part 60, appendix A. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus 0.5 min.

8.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculations of concentrations.

8.4 Preparation of Collection Train.

8.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon™ film or aluminum foil until just prior to assembly or until sampling is about to begin.

8.4.2 Place 100 ml of water in each of the first two impingers, and leave the third impinger empty. If additional capacity is required for high expected concentrations of formaldehyde in the stack gas, 200 ml of water per impinger may be used or additional impingers may be used for sampling. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Care should be taken to ensure that the silica gel is not entrained and carried out from the impinger during sampling. 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.

8.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring when stack temperatures are < 260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 for details. Other connection systems utilizing either 316 stainless steel or Teflon™ ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.4.4 Assemble the train as shown in Figure 1. During assembly, a very light coating of silicone grease may be used on ground-glass joints of the impingers, but the silicone grease should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon™ tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.

8.4.5 Place crushed ice all around the impingers.

8.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

8.5 Leak-Check Procedures.

8.5.1 Pre-test Leak-check: Recommended, but not required. If the tester elects to conduct the pre-test leak-check, the following procedure shall be used.

8.5.1.1 After the sampling train has been assembled, turn on and set probe heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Viton-a O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in Hg) vacuum.

NOTE: A lower vacuum may be used, provided that the lower vacuum is not exceeded during the test.

If a woven glass fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in Hg) vacuum. (A lower vacuum may be used if this lower vacuum is not exceeded during the test.) Next connect the probe to the train and leak-check at about 25 mm Hg (1 in Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in Hg) vacuum. Leakage rates in excess of (a) 4 percent of the average sampling rate or (b) 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

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

8.5.1.3 When the leak-check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the third impinger.

8.5.2 Leak-checks During Sampling Run:

8.5.2.1 If, during the sampling run, a component change (e.g., impinger) becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure described in Section 10.3.3, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.0057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

NOTE: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

8.5.2.2 Immediately after component changes, leak-checks are optional. If performed, the procedure described in section 8.5.1.1 shall be used.

8.5.3 Post-test Leak-check:

8.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as the pre-test leak-check, except that the post-test leak-check shall be conducted at a vacuum

greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

8.6 Sampling Train Operation.

8.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic, below 28 l/min (1.0 cfm). Maintain a temperature around the probe of 120°C ± 14°C (248° ± 25°F).

8.6.2 For each run, record the data on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant adjustments (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the probe heating system are at the specified temperature, and verify that the Pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S Pitot tube coefficient is 0.84 ± 0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 details the procedure for using the nomographs. If the stack gas molecular weight and the Pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

8.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, a low vacuum on the train may have to be started prior to entering the stack.

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

8.6.6 Traverse the stack cross section, as required by EPA Method 1, 40 CFR part 60, appendix A, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

8.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of < 20°C (68°F) at the silica gel outlet.

8.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. An additional train or trains may also be used for sampling when the capacity of a single train is exceeded.

8.6.9 When two or more trains are used, separate analyses of components from each train shall be performed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

8.6.10 At the end of the sampling run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Also, check the Pitot lines as described in EPA Method 2, 40 CFR part 60, appendix A. The lines must pass this leak-check in order to validate the velocity-head data.

8.6.11 Calculate percent isokineticity (see Method 2) to determine whether the run was valid or another test should be made.

8.7 Sample Preservation and Handling.

8.7.1 Samples from most sources applicable to this method have acceptable holding times using normal handling practices (shipping samples iced, storing in refrigerator at 2°C until analysis). However, forming section stacks and other sources using waste water sprays may be subject to microbial contamination. For these sources, a biocide (quaternary ammonium compound solution) may be added to collected samples to improve sample stability and method ruggedness.

8.7.2 Sample holding time: Samples should be analyzed within 14 days of collection. Samples must be refrigerated/kept cold for the entire period preceding analysis. After the samples have been brought to room temperature for analysis, any analyses needed should be performed on the same day. Repeated cycles of warming the samples to room temperature/refrigerating/rewarming, then analyzing again, etc., have not been investigated in depth to evaluate if analyte levels remain stable for all sources.

8.7.3 Additional studies will be performed to evaluate whether longer sample holding times are feasible for this method.

8.8 Sample Recovery.

8.8.1 Preparation:

8.8.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tightly while the sampling train is cooling because a vacuum will be created, drawing liquid from the impingers back through the sampling train.

8.8.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon™ caps, or caps of other inert materials may be used to seal all openings.

8.8.1.3 Transfer the probe and impinger assembly to an area that is clean and protected from wind so that the chances of contaminating or losing the sample are minimized.

8.8.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

8.8.1.5 Save a portion of the washing solution (high purity water) used for cleanup as a blank.

8.8.2 Sample Containers:

8.8.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest ml, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the combined impinger solution from the graduated cylinder into the polyethylene bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first three impingers, and impinger connectors) with water. Use less than 400 ml for the entire waste (250 ml would be better, if possible). Add the rinse water to the sample container.

8.8.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with water from a wash bottle. Brush with a bristle brush and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok (or equivalent) fitting with water in a similar way.

8.8.2.1.2 Rinse the probe liner with water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a bristle brush. Hold the probe in an inclined position, and squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. Rinse the brush with water and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as describe above.

NOTE: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

8.8.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of water for each rinse, and brush each surface to which the sample is exposed with a bristle brush to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush, using water.

8.8.2.1.4 After all water washing and particulate matter have been collected in the sample container, tighten the lid so the sample will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

8.8.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

8.8.2.2 Container 2: Sample Blank. Prepare a blank by using a polyethylene container and adding a volume of water equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

8.8.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon™ caps maybe used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

8.8.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice. Putting sample bottles in Zip-Lock™ bags can aid in maintaining the integrity of the sample labels. Sample containers should be placed vertically to avoid leakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory. It is critical that samples be chilled immediately after recovery. If the source is susceptible to microbial contamination from wash water (e.g. forming section stack), add biocide as directed in section 8.2.5.

8.8.2.5 A quaternary ammonium compound can be used as a biocide to stabilize samples against microbial degradation following collection. Using the stock quaternary ammonium compound (QAC) solution; add 2.5 ml QAC solution for every 100 ml of recovered sample volume (estimate of volume is satisfactory) immediately after collection. The total volume of QAC solution must be accurately known and recorded, to correct for any dilution caused by the QAC solution addition.

8.8.3 Sample Preparation for Analysis

8.8.3.1 The sample should be refrigerated if the analysis will not be performed on the day of sampling. Allow the sample to warm at room temperature for about two hours (if it has been refrigerated) prior to analyzing.

8.8.3.2 Analyze the sample by the pararosaniline method, as described in Section 11. If the color-developed sample has an absorbance above the highest standard, a suitable dilution in high purity water should be prepared and analyzed.

9. Quality Control.

9.1 Sampling: See EPA Manual 600/4-77-02b for Method 5 quality control.

9.2 Analysis: The quality assurance program required for this method includes the analysis of the field and method blanks, and procedure validations. The positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

9.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recover water, and water reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train must be heated during the sample test. The train will be recovered as if it were an actual test sample. No

gaseous sample will be passed through the blank sampling train.

9.2.2 Blank Correction: The field blank formaldehyde concentrations will be subtracted from the appropriate sample formaldehyde concentrations. Blank formaldehyde concentrations above 0.25 µg/ml should be considered suspect, and subtraction from the sample formaldehyde concentrations should be performed in a manner acceptable to the Administrator.

9.2.3 Method Blanks: A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

10. Calibration.

10.1 Probe Nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in). When the nozzle becomes nicked or corroded, it shall be repaired and calibrated, or replaced with a calibrated nozzle before use. Each nozzle must be permanently and uniquely identified.

10.2 Pitot Tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded and if it meets design and intercomponent spacing specifications.

10.3 Metering System.

10.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not delete leakages with the pump. For these cases, the following leak-check procedure will apply: make a ten-minute calibration run at 0.00057 m^3/min (0.02 cfm). At the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

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

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

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

10.4 Probe Heater: The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

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

10.6 Barometer: Adjust the barometer initially and before each test series to agree to within ± 2.5 mm Hg (0.1 in Hg) of the mercury barometer. Alternately, if a National Weather Service Station (NWSS) is located at the same altitude above sea level as the test site, the barometric pressure reported by the NWSS may be used.

10.7 Balance: Calibrate the balance before each test series, using Class S standard weights. The weights must be within ± 0.5 percent of the standards, or the balance must be adjusted to meet these limits.

11.0 Procedure for Analysis.

The working formaldehyde standards (0.25, 0.50, 1.0, 2.0, and 3.0 µg/ml) are analyzed and a calibration curve is calculated for each day's analysis. The standards should be analyzed first to ensure that the method is working properly prior to analyzing the samples. In addition, a sample of the high-purity water should also be analyzed and used as a "0" formaldehyde standard.

The procedure for analysis of samples and standards is identical: Using the pipet set to 2.50 ml, pipet 2.50 ml of the solution to be analyzed into a polystyrene cuvette. Using the 250 µl pipet, pipet 250 µl of the pararosaniline reagent solution into the cuvette. Seal the top of the cuvette with a Parafilm square and shake at least 30 seconds to ensure the solution in the cuvette is well-mixed. Peel back a corner of the Parafilm so the next reagent can be added. Using the 250 µl pipet, pipet 250 µl of the sodium sulfite reagent solution into the cuvette. Reseal the cuvette with the Parafilm, and again shake for about 30 seconds to mix the solution in the cuvette. Record the time of addition of the sodium sulfite and let the color develop at room temperature for 60 minutes. Set the spectrophotometer to 570 nm and set to read in Absorbance Units. The spectrophotometer should be equipped with a holder for the 1-cm pathlength cuvettes. Place cuvette(s) containing high-purity water in the spectrophotometer and adjust to read 0.000 AU.

After the 60 minutes color development period, read the standard and samples in the spectrophotometer. Record the absorbance reading for each cuvette. The calibration curve is calculated by linear regression, with the formaldehyde concentration as the "x" coordinate of the pair, and the absorbance reading as the "y" coordinate. The procedure is very reproducible, and typically will yield values similar to these for the calibration curve:

Correlation Coefficient: 0.9999

Slope: 0.50

Y-Intercept: 0.090

The formaldehyde concentration of the samples can be found by using the trendline feature of the calculator or computer program used for the linear regression. For example, the TI-55 calculators use the "X" key (this gives the predicted

formaldehyde concentration for the value of the absorbance you key in for the sample). Multiply the formaldehyde concentration from the sample by the dilution factor, if any, for the sample to give the formaldehyde concentration of the original, undiluted, sample (units will be micrograms/ml).

11.1 Notes on the Pararosaniline Procedure

11.1.1 The pararosaniline method is temperature-sensitive. However, the small fluctuations typical of a laboratory will not significantly affect the results.

11.1.2 The calibration curve is linear to beyond 4 µg/ml formaldehyde, however, a research-grade spectrophotometer is required to reproducibly read the high absorbance values. Consult your instrument manual to evaluate the capability of the spectrophotometer.

11.1.3 The quality of the laboratory water used to prepare standards and make dilutions is critical. It is important that the cautions given in the Reagents section be observed. This procedure allows quantitation of formaldehyde at very low levels, and thus it is imperative to avoid contamination from other sources of formaldehyde and to exercise the degree of care required for trace analyses.

11.1.4 The analyst should become familiar with the operation of the Oxford or equivalent pipettors before using them for an analysis. Follow the instructions of the manufacturer; one can pipet water into a tared container on any analytical balance to check pipet accuracy and precision. This will also establish if the proper technique is being used. Always use a new tip for each pipetting operation.

11.1.5 This procedure follows the recommendations of ASTM Standard Guide D 3614, reading all solutions versus water in the reference cell. This allows the absorbance of the blank to be tracked on a daily basis. Refer to ASTM D 3614 for more information.

12.0 Calculations.

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

12.1 Calculations of Total Formaldehyde.

12.1.1 To determine the total formaldehyde in mg, use the following equation if biocide was *not* used:

Total mg formaldehyde =

$$C_d \, x V \, x \, DF \, x \, 0.001 mg/\mu g$$

where:

C_d = measured conc. formaldehyde, µg/ml

V = total volume of stack sample, ml

DF= dilution factor

12.1.2 To determine the total formaldehyde in mg, use the following equation if biocide was used:

Total mg formaldehyde =

$$\frac{C_d \, x V}{(V - B) \, x \, DF \, x \, 0.001 mg/\mu g}$$

Where:

C_d = measured conc. formaldehyde, µg/ml

V = total volume of stack sample, ml

B = total volume of biocide added to sample, ml

DF = dilution factor

12.2 Formaldehyde concentration (mg/m^3) in stack gas. Determine the formaldehyde concentration (mg/m^3) in the stack gas using the following equation:

Formaldehyde concentration (mg/m^3) =

$$\frac{K \, x \, [total \ formaldehyde, mg]}{V_m(std)}$$

where:

K = 35.31 cu ft/m^3 for V_m(std) in English units, or

K = 1.00 m^3/m^3 for V_m(std) in metric units

V_m(std) = volume of gas sample measured by a dry gas meter, corrected to standard conditions, dscm (dscf)

12.3 Average dry gas meter temperature and average orifice pressure drop are obtained from the data sheet.

12.4 Dry Gas Volume: Calculate V_m(std) and adjust for leakage, if necessary, using the equation in Section 6.3 of EPA Method 5, 40 CFR part 60, appendix A.

12.5 Volume of Water Vapor and Moisture Content: Calculated the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA Method 5.

13.0 Method Performance.

The precision of this method is estimated to be better than ± 5 percent, expressed as ± the percent relative standard deviation.

14.0 Pollution Prevention. (Reserved)

15.0 Waste Management. (Reserved)

16.0 References.

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J.F. Walker, FORMALDEHYDE, Third Edition, 1964.

US EPA 40 CFR, Part 60, Appendix A, Test Methods 1-5