



## Standard Test Method for Determining Formaldehyde Concentration in Air from Wood Products Using a Small Scale Chamber<sup>1</sup>

This standard is issued under the fixed designation D 6007; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method measures the formaldehyde concentrations in air from wood products under defined test conditions of temperature and relative humidity. Results obtained from this small-scale chamber test method are intended to be comparable to results obtained testing larger product samples by the large chamber test method for wood products, Test Method E 1333. The results may be correlated to values obtained from Test Method E 1333. The quantity of formaldehyde in an air sample from the small chamber is determined by a modification of the National Institute for Occupational Safety and Health (NIOSH) 3500 chromotropic acid test procedure. Other analytical procedures may be used to determine the quantity of formaldehyde in the air sample provided that such methods give results comparable to those obtained by using the chromotropic acid procedure. However, the test results and test report must be properly qualified and the analytical procedure employed must be accurately described.

1.2 The wood-based panel products to be tested by this test method are characteristically used for different applications and are tested at different relative amounts or loading ratios to reflect different applications. This is a test method that specifies testing at various loading ratios for different product types. However, the test results and test report must be properly qualified and must specify the make-up air flow, sample surface area, and chamber volume.

1.3 Ideal candidates for small-scale chamber testing are products relatively homogeneous in their formaldehyde release characteristics. Still, product inhomogeneities must be considered when selecting and preparing samples for small-scale chamber testing.

1.4 The values stated in SI units are the standard values. Any values given in parentheses are for information only.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 3195 Practice for Rotameter Calibration<sup>2</sup>
- D 5197 Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)<sup>2</sup>
- D 5221 Test Method for Continuous Measurement of Formaldehyde in Air<sup>2</sup>
- E 77 Test Methods for Inspection and Verification of Thermometers<sup>3</sup>
- E 220 Method for Calibration of Thermocouples by Comparison Techniques<sup>3</sup>
- E 337 Test Method for Measuring Humidity with a Psychrometer (the Measurement of Wet-Bulb and Dry-Bulb Temperatures)<sup>2</sup>
- E 741 Test Method for Determining Air Change in a Single Zone by Means of Tracer Gas Dilution<sup>4</sup>
- E 1333 Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Under Defined Test Conditions Using a Large Chamber<sup>4</sup>

#### 2.2 U.S. Department of Housing and Urban Development (HUD) Standards:

- 24 CFR 3280, Manufactured Home Construction and Safety Standards<sup>5</sup>

#### 2.3 NIOSH Standard:

- 3500 Formaldehyde Method<sup>6</sup>

#### 2.4 Other Documents:

- Minnesota Statutes Section 144.495, 325f.18, and 325F.181 Formaldehyde Gases in Building Materials<sup>7</sup>

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *air change rate, N* ( $N$  is equal to  $Q/V$ )—the ratio of conditioned and filtered air that enters or is replaced in the small chamber in one hour divided by the interior volume of the small chamber, air changes per hour (ACH).

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.03.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.03.

<sup>4</sup> Annual Book of ASTM Standards, Vol 04.07.

<sup>5</sup> Federal Register, Vol 49, No. 155, Aug. 8, 1984, available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

<sup>6</sup> U.S. Dept. of Health and Human Services, 1989, available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

<sup>7</sup> Available from Print Communications, Dept. of Administration, 117 University Ave., St. Paul, MN 55155.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-7 on Wood and is the direct responsibility of Subcommittee D07.03 on Panel Products.

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3.1.2 *equilibrium concentration*,  $C_{eq}$ —is that  $C_s$  measured when  $Q$  equals zero, ppm.

3.1.3 *loading ratio*,  $L$ —( $L$  is equal to  $A/V$ ) the total exposed surface area, excluding panel edges, of the product being tested divided by the test chamber's interior volume,  $m^2/m^3$ .

3.1.4 *make-up air flow*,  $Q$ —the quantity of conditioned and filtered air fed into the chamber per unit time,  $m^3/h$ .

3.1.5 *mass transfer coefficient*,  $K$ —a measure of the permeability of the emitting surface of a wood based panel product, m/h.  $K$  is calculated as follows:<sup>8</sup>

$$K = \frac{(Q/A)(C_s)}{(C_{eq} - C_s)} \quad (1)$$

3.1.6 *N/L ratio*—( $N/L$  is equivalent to  $Q/A$ ) the ratio of air flow through the chamber to sample surface area, m/h, as follows:

$$N/L = \frac{Q/V}{A/V} = (Q/V) \times (V/A) = Q/A \quad (2)$$

3.1.7 *Q/A ratio*—the ratio of air flow through the chamber ( $Q$ ) to sample surface area ( $A$ ), m/h.

3.1.8 *sample surface area*,  $A$ —the total area of all sample faces exposed in the chamber,  $m^2$ .

3.1.9 *steady state concentration*,  $C_s$ —the interval when the formaldehyde concentration is not changing with time (expressed in parts of formaldehyde per million parts air (ppm)) under the defined environmental test parameters.

3.1.10 *volume of closed system*,  $V$ —the interior volume of the test chamber,  $m^3$ .

#### 4. Significance and Use

4.1 Limitations on formaldehyde levels have been established for wood panel building products made with urea-formaldehyde adhesives and permanently installed in homes or used as components in kitchen cabinets and similar industrial products. This test method is intended for use in conjunction with the test method referenced by HUD Rules and Regulations 24 CFR 3280 for manufactured housing and by Minnesota Statutes Section 144.495 for housing units and building materials. This test method provides a means of testing smaller samples and reduces the time required for testing.

4.2 Formaldehyde concentration levels obtained by this small-scale method may differ from expected in full-scale indoor environments. Variations in product loading, temperature, relative humidity, and air exchange will affect formaldehyde emission rates and thus likely indoor air formaldehyde concentrations.

4.3 This test method requires the use of a chamber of 0.02 to 1  $m^3$  in volume to evaluate the formaldehyde concentration in air using the following controlled conditions:

4.3.1 Conditioning of specimens prior to testing,

4.3.2 Exposed surface area of the specimens in the test chamber,

4.3.3 Test chamber temperature and relative humidity,

4.3.4 The Q/A ratio, and

4.3.5 Air circulation within the chamber.

#### 5. Interferences

5.1 The NIOSH 3500 analytical method lists phenols as a negative interference when present at an 8:1 excess over formaldehyde. Modifications in the analytical procedure shall be made when relatively high phenol to formaldehyde concentrations (8:1) are anticipated.<sup>9, 10</sup>

#### 6. Apparatus

6.1 *Test Chamber*—The interior volume of the small chamber shall be from 0.02 to 1  $m^3$ . The interior of the test chamber shall be free of refrigeration coils that condense water and items such as humidifiers with water reservoirs since water has the potential for collecting formaldehyde and thus influencing test results. The interior surfaces of the small chamber, including any sample support system, shall be a nonadsorbent material. Stainless steel, aluminum, and polytetrafluoroethylene (PTFE) have been found appropriate as chamber lining materials. All joints except for doors used for loading and unloading specimens should be sealed. Doors shall be self-sealing.

6.2 *Make-Up Air*:

6.2.1 The make-up air shall come from a filtered dust-free environment and contain not more than 0.02 ppm of formaldehyde. This can be accomplished by passing make-up air through a filter bed of activated carbon, activated alumina impregnated with potassium permanganate, or other materials capable of absorbing, or oxidizing formaldehyde.

6.2.2 Make-up air for the chamber must pass through a calibrated air flow measuring device.

6.2.3 *Air Circulation*—Low speed mixing fans or multi-port inlet and outlet diffusers are two techniques that have been used successfully to ensure mixing of the chamber air over all sample surfaces.

6.2.4 *Air Sampling Port*—The exhaust flow (that is, chamber outlet) is normally used as the sampling point, although separate sampling ports in the chamber can be used. The sampling system shall be constructed of a material to minimize adsorption (for example, glass, stainless steel), and the system should be maintained at the same temperature as the test chambers.

6.3 Examples of acceptable reagents, materials, and equipment are provided in Appendix X1.

#### 7. Hazards

7.1 *Chromotropic Acid Reagent Treatment*—(See 10.3.4 and 10.3.5.) During this hazardous operation, the operator must wear rubber gloves, apron, and a full face mask or be protected from splashing by a transparent shield such as a hood window. The solution becomes extremely hot during addition of sulfuric acid. If acid is not added slowly, some loss of sample could occur due to splattering.

<sup>9</sup> Hakes, D., Johnson, G., and Marhevka, J., *Procedure for Elimination of Phenol Interference in the Chromotropic Acid Method for Formaldehyde*, American Industrial Hygiene Association, April 1984.

<sup>10</sup> *Technical Bulletin No. 415*, National Council of the Paper Industry for Air and Stream Improvement Inc. (NCASI), 1983.

<sup>8</sup> Christensen, R. L., and Anderson, W. H., *Measuring Formaldehyde Concentrations Using a Small Scale Chamber*, Proceedings 23rd International Particleboard/Composite Materials Symposium, W.S.U., 1989.

7.2 *Cleaning Chemicals for Glassware*— Use appropriate precautions if cleaning chemicals are considered to be hazardous.

## 8. Test Specimens

8.1 *Standard Face and Back Configuration*—Loading ( $L$  or  $A/V$ ) is defined as the total exposed specimen surface area, excluding edge area, divided by the chamber volume. Aluminum tape shall be used to cover the edges of the specimens if the edge exposure is greater than 5 % of the surface area, thereby retarding formaldehyde emission from the edge. The  $Q/A$  ratios in Table 1 are used for testing wood panel products containing formaldehyde. Each small chamber will have a unique value for the make-up air flow ( $Q$ ) dependent on the sample surface area used, and the type of product tested.

8.2 *Nonstandard Sample Configuration Testing Products with Single Surface Exposed*—Some products have significantly different formaldehyde release characteristics for each surface. In those cases, panels may be tested back-to-back with edges taped together. The panels shall be identified as tested in the back-to-back mode.

8.3 *Combination Testing*—Different products may be tested in combination. Qualify the test report and note the  $Q/A$  ratio used.

## 9. Sample Material Handling and Specimen Conditioning

9.1 *Handling*—Materials selected for testing shall be wrapped in polyethylene plastic having a minimum thickness of 0.15 mm (6 mil) until sample conditioning is initiated. When testing wood products that are not newly manufactured such as after original application, installation or use, the method of packaging and shipping the products for testing shall be fully described. Information on the age and history of the product shall be detailed in the test report.

9.2 *Conditioning*—Condition test specimens with a minimum distance of 0.15 m (6 in.) between each specimen for 2 h  $\pm$  15 min at conditions of 24  $\pm$  3°C (75  $\pm$  5°F) and 50  $\pm$  5 % relative humidity. The formaldehyde concentration in the air within 0.3 m (12 in.) of where panels are conditioned shall be not more than 0.1 ppm during the conditioning period. Alternative conditioning intervals may give better correlation, such as seven day conditioning that parallels Test Method E 1333.

## 10. Procedure

### 10.1 Test Procedure for Materials:

10.1.1 Purge the chamber by running empty or with the use of filters designed to reduce the formaldehyde background concentration in air, or both. The formaldehyde background

concentration in air of the empty operating chamber shall not exceed 0.02 ppm. Clean chamber surfaces with water or suitable solvent if formaldehyde background concentrations approach 0.02 ppm.

10.1.2 Locate the specimens in the chamber so that the conditioned air stream circulates over all panel surfaces.

10.1.3 Operate the chamber at 25  $\pm$  1°C (77  $\pm$  2°F) and 50  $\pm$  4 % relative humidity. Record the temperature, relative humidity, and barometric pressure during the testing period. Conduct the chamber test at a given  $Q/A$  ratio and record this ratio in the report.

10.1.4 Specimens remain in the operating chamber until a steady state formaldehyde concentration is reached. The time may be estimated using the following equation:

$$t = \frac{-1n(1 - C_t/C_s)V}{Q + KA} \quad (3)$$

where:

- $t$  = time to any percent of  $C_s$  less than 100 % (such as 99.999999999 etc.),
- $C_t$  = concentration at time,  $t$ ,
- $C_s$  = steady state formaldehyde concentration,
- $A$  = product surface area,  $m^2$ ,
- $V$  = chamber volume,  $m^3$ ,
- $K$  = mass transfer coefficient, m/h, and
- $-1n$  = negative natural log.

It is necessary to know the range of  $K$  for the product involved. If  $K$  is unknown, a conservative estimate based on the literature may be used.<sup>8</sup> Alternatively, back to back air tests giving replicate values within the error of the analytical method may be used.

10.2 *Air Sampling*—Purge air sampling lines for 1 min. At the sampling station, bubble air through a single impinger containing 20 mL of a 1 % sodium bisulfite ( $NaHSO_3$ ) solution. A filter trap may be placed between the impinger and the flowmeter. Set a calibrated flowmeter to maintain an average airflow of 1  $\pm$  0.05 L/min. for 30 min. with time measured accurately to within 5 s. Following air sampling, analyze the collection solution.

### 10.3 Analysis of Air Samples:

10.3.1 Pipet 4 mL of the  $NaHSO_3$  solution from the impinger into each of three 16 by 150-mm screwcap test tubes for triplicate analysis of each impinger sample.

10.3.2 Pipet 4 mL of 1 %  $NaHSO_3$  into a 16 by 150-mm screwcap test tube to act as a reagent blank.

10.3.3 Add 0.1 mL of 1 % chromotropic acid reagent to each test tube. Shake tube after addition.

10.3.4 Slowly and carefully pipet 6.0 mL concentrated sulfuric acid ( $H_2SO_4$ ) into each test tube ( **Precaution**—See 7.1.) and allow to flow down the side of test tube. Allow the volumetric pipet to drain. *Do not blow out.* Before placing caps on test tubes, check the condition of the polytetrafluoroethylene (PTFE) cap liners to make sure they are clean and not deteriorated.

10.3.5 Slowly and gently agitate test tubes to affect mixing. Mixing is complete when there is no sign of stratification. Caution needs to be taken due to the exothermic chemical reaction. Rapid mixing will cause heating and a pressure

**TABLE 1**  $Q/A$  Ratios,  $\pm 2$  %

Test Method E 1333 L ( $m^2/m^3$ )	N/L or $Q/A$ (m/h)	Product Type
0.95	0.526	hardwood plywood wall paneling
0.43	1.173	particleboard flooring panels, industrial particleboard panels, industrial hardwood plywood panels
0.26	1.905	medium density fiberboard (MDF)
0.13	3.846	particleboard door core

increase which may break the test tube. Vent test tubes to release pressure.

10.3.6 If absorbance readings exceed 1.0 or if spectrophotometric analysis is performed within 2 h, heat capped test tubes to 95°C or place capped test tubes in a boiling water bath for 15 ± 2 min. to ensure that the chemical reaction is completed. Remove tubes from water bath and allow to cool to room temperature.

#### 10.4 Absorbance Readings:

10.4.1 Standardize the spectrophotometer using distilled water at 580 nm in accordance with the instrument's operating instructions. The reagent blank shall be read against distilled water because an absorbance above 0.100 for the reagent blank indicates contamination of reagent blank or improper solution preparation. If absorbance for the reagent blank compared to distilled water is greater than 0.100, repeat the entire standardization procedure.

10.4.2 Zero the instrument using the reagent blank if the absorbance is not greater than 0.100 (compared to distilled water as zero). Alternatively, the instrument may be left zeroed on distilled water, and the absorbance of the reagent blank subtracted from the absorbance of the standard solutions.

10.4.3 Read and record absorbance at 580 nm for each test tube prepared (see A4.6-A4.9). If the absorbance of the specimen solution is found to fall outside the preferred absorbance range (>1.0), steps 10.3.1-10.3.4 may be repeated using an appropriate dilution of each impinger solution.

## 11. Calculation

11.1 Convert the volume of air sampled to the volume of air at standard conditions as follows:

$$V_s = \frac{V \times P \times 298}{101 \times (T + 273)} \quad (4)$$

where:

$V_s$  = volume of air at standard conditions (101 kPa and 298 K), L,

$V$  = volume of air sampled, L,

$P$  = barometric pressure, kPa, and

$T$  = temperature of sample air, °C.

11.2 Calculate total micrograms of formaldehyde collected in each impinger sample as follows:

$$C_t = C_a \times F_a \quad (5)$$

where:

$C_t$  = total formaldehyde in the sample, mg,

$C_a$  = total quantity of formaldehyde in the sample aliquots taken from the impinger (as determined from the calibration curve in Annex A4), mg, and

$F_a$  = aliquot factor =  $\frac{\text{sampling solution volume, mL}}{\text{aliquot used, mL}}$

11.2.1 Calculate the concentration of formaldehyde in air in the small chamber as follows:

$$C_s = \frac{C_t \times 24.47}{V_s \times 30.03} \quad (6)$$

where:

$C_s$  = parts of formaldehyde per million parts air, ppm,

30.03 = molecular weight of formaldehyde, and

24.47 = μL of formaldehyde gas in 1 μmol at 101 kPa and 298 K.

Round calculated formaldehyde concentrations to the nearest 0.01 ppm. Round up to the nearest 0.01 ppm any value at or in excess of 0.005 ppm. Round down all values below 0.005 to the nearest 0.01 ppm.

11.3 When the chamber temperature differs from 25 by ¼ °C (77 by ½ °F) or more, adjust the formaldehyde concentrations obtained to a standard temperature of 25°C (77°F) using a formula developed by Berge, et al.<sup>11</sup> Annex A1 contains a table of conversion factors for use at different observed test temperatures as calculated using this formula. The observed test temperature is the average temperature for the total period of 15 min prior to air sampling plus the time of air sampling.

11.4 The small chamber formaldehyde concentration in air shall be adjusted to a concentration at 50 % relative humidity when the difference in relative humidity from 50 % is greater than or equal to 1 % (see Annex A2).

## 12. Report

12.1 Report the following information:

12.1.1 Test number.

12.1.2 Title of report shall state if standard face and back configuration testing (see 8.1) or if nonstandard configuration testing (see 8.2) was performed.

12.1.3 The manner in which materials were shipped or stored, or both: wrapped separately in vapor retarder, wrapped collectively in vapor retarder or in original box or container. If materials were shipped unwrapped, or not in the original box or container, it shall be noted in the test report. Information on age and product history, if known, shall be described in the test report.

12.1.4 Name of product manufacturer or name of company submitting material, or both, date of manufacture, and sampling date (if known).

12.1.5 Description of test material or product shall include generic product name, thickness, size, if surface is finished or sealed (both surfaces should be described), and special treatment (if known).

12.1.6 Specimen conditioning details to include average temperature and range (nearest ¼ °C), average relative humidity and range (nearest 1 %), and time to the nearest minute.

12.1.7 Formaldehyde background concentration in the air in the area where specimens are conditioned (rounded to the nearest 0.01 ppm).

12.1.8 Chamber volume: nominal length, width, and height.

12.1.9 Chamber  $Q/L$  ratio.

12.1.10 Description of specimens as loaded into chamber including number of specimens in charge and number of surfaces exposed.

12.1.11 Average temperature and range (nearest ¼ °C), average relative humidity and range (nearest 1 %), and time to the nearest minute during the sampling period.

<sup>11</sup> Berge, A., Mellagaard, B., Hanetho, P., and Ormstad, E. B., *Formaldehyde Release from Particleboard-Evaluation of a Mathematical Model*, Holz Als Roh-und Werkstoff 38, 1980, pp. 252-255.

12.1.12 Chamber formaldehyde concentration in air at test conditions; chamber formaldehyde concentration in air corrected to 25°C, 50 % relative humidity, rounded to nearest 0.01 ppm.

12.1.13 The analytical method employed if different from the NIOSH 3500 chromotropic acid test procedure.

12.1.14 Formaldehyde background concentration of air in chamber prior to test and formaldehyde concentration of make-up air (rounded to the nearest 0.01 ppm).

12.1.15 Air-sampling rate and length of sample time.

12.1.16 Date of test.

**13. Precision and Bias**

13.1 *Precision*—The precision of the procedure in this test

method for measuring the formaldehyde concentrations in air from wood products using a small-scale chamber is being determined.

13.2 *Bias*—Since there is no acceptable reference material suitable for determining the bias for the procedure in this test method, no statement on bias is being made.

**14. Keywords**

14.1 airborne; chromotropic acid analysis; formaldehyde concentration in air; small chamber; small-scale test; wood products

**ANNEXES**

**(Mandatory Information)**

**A1. TEMPERATURE CONVERSION FACTORS FOR FORMALDEHYDE**

A1.1 Table A1.1 is based on the Berge, et al<sup>11</sup> formula to correct formaldehyde concentrations in air for temperature:

$$C = C_o \times e^{-R(1/t-1/t_o)}$$

or

$$C_o = C e^{R(1/t-1/t_o)}$$

where:

- $C$  = test formaldehyde concentration level,
- $C_o$  = corrected formaldehyde concentration level,
- $e$  = natural log base,
- $R$  = coefficient of temperature (9799),
- $t$  = actual temperature, K, and
- $t_o$  = corrected temperature, K.

**TABLE A1.1 Temperature Conversion Table for Formaldehyde**

NOTE 1—The Berge, et al<sup>11</sup> equation is an exponential function. The greater the variance between actual and corrected temperature, the greater the potential error. Two horizontal lines within the table delineate the specified test temperature ranges 25 ± 1°C (77 ± 2°F).

Actual		To Convert to 25°C (77°F) Multiply by	Actual		To Convert to 25°C (77°F) Multiply by
°C	(°F)		°C	(°F)	
22.2	(72)	1.36	25.3	(77.5)	0.97
22.5	(72.5)		25.6	(78)	
22.8	(73)		25.8	(78.5)	
23.1	(73.5)	1.24	26.1	(79)	0.89
23.3	(74)	1.20	26.4	(79.5)	0.86
23.6	(74.5)		26.7	(80)	
23.9	(75)	1.13	26.9	(80.5)	0.81
24.2	(75.5)		27.2	(81)	
24.4	(76)	1.06	27.5	(81.5)	0.76
24.7	(76.5)		27.8	(82)	
25.0	(77)	1.00			

## A2. RELATIVE HUMIDITY CONVERSION FACTORS FOR FORMALDEHYDE

A2.1 Table A2.1 is based on the Berge, et al<sup>11</sup> formula to correct formaldehyde concentrations in air for relative humidity:

$$C = C_o [1 + A(H - H_o)]$$

or

$$C_o = \frac{C}{1 + A(H - H_o)}$$

**TABLE A2.1 Relative Humidity Conversion Table for Formaldehyde**

Actual RH %	To Convert to 50 % RH Multiply by	Actual RH %	To Convert to 50 % RH Multiply by
46	1.08	51	0.98
47	1.06	52	0.97
48	1.04	53	0.95
49	1.02	54	0.93
50	1.00		

where:

$C$  = test formaldehyde concentration level,  
 $C_o$  = corrected formaldehyde concentration level,  
 $A$  = coefficient of humidity (0.0175),  
 $H$  = actual relative humidity, and  
 $H_o$  = relative humidity, %.

## A3. STANDARD SOLUTIONS A AND B

A3.1 *Standardization of Formaldehyde Standard Solution A (1.0 mg/mL):*

A3.1.1 Pipet 2.70 mL of 37.0 % formaldehyde solution into a 1 L volumetric flask. Dilute to mark with freshly distilled water and mix well. This solution is stable for at least one month.

A3.1.2 Calibrate the pH meter with standard buffer solution of pH 9.0.

A3.1.3 Pipet two 50 mL aliquots of formaldehyde standard Solution A into two 150-mL beakers for duplicate analysis and add 20 mL of 1 M sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) to each beaker. Sodium sulfite solution can age, thus the 1 M sodium sulfite solution should be adjusted to a 9.5 pH before adding to standard Solution A aliquots.

A3.1.4 Place solution on magnetic stirrer. Immerse pH electrodes into the solution and carefully titrate with 0.100 N hydrochloric acid (HCl) to the original pH of the solution. Record volume of HCl and corresponding pH intermittently. Make a graph of pH versus volume of HCl.

A3.1.5 Calculate the concentration,  $C_A$ , of formaldehyde standard Solution A in milligrams per millilitre as follows:

$$C_A = \frac{V \times N \times 30.03 \text{ (mg per milliequivalent)}}{50 \text{ (mL)}}$$

where:

$V$  = 0.100 N HCl required at pH of 9.5 from the graph prepared in A3.1.4, mL, and  
 $N$  = normality of HCl. The concentration of standard Solution A will be the average of the two analyses conducted.

A3.2 *Standard Solution B:*

A3.2.1 Prepare formaldehyde standard Solution B by diluting 1 mL of standard Solution A and 1 g of sodium bisulfite ( $\text{NaHSO}_3$ ) to 100 mL in a volumetric flask using distilled water. This standard is stable for at least one week.

A3.2.2 Calculate the concentration of formaldehyde  $C_B$  in standard Solution B in micrograms per millilitre as follows:

$$C_b = \frac{C_A \times 1000 \times 1 \text{ mL}}{100}$$

A3.2.3 Record the value.

## A4. CALIBRATION CURVE

A4.1 Prepare a 1 % sodium bisulfite ( $\text{NaHSO}_3$ ) solution by dissolving 1 g of  $\text{NaHSO}_3$  in a 100 mL volumetric flask and diluting to the mark with distilled water. This solution is stable at room temperature and should be prepared on a weekly basis.

A4.2 Label six 16 by 150 mm screwcapped test tubes 1, 2, 3, 4, 5, and 6.

A4.3 Pipet the following volumes of 1 % sodium bisulfite solution and then standard Solution B (see Annex A3) into the labeled test tubes:

Tube No.	$\text{NaHSO}_3$	Volume, mL	Solution B
1	4.0		0
2	3.9		0.10
3	3.7		0.30
4	3.5		0.50
5	3.3		0.70
6	3.0		1.00

A4.3.1 Note that no Solution B was added to Test Tube 1. Test Tube 1 will be the reagent blank.

A4.4 Add 0.1 mL of 1 % chromotropic acid reagent to each

test tube. Shake tube after addition.

A4.5 Slowly and carefully pipet 6.0 mL concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) into each test tube (**Precaution**—See 7.1.) and allow to flow down the side of the test tube. Allow the volumetric pipet to drain. *Do not blow out.* Before placing caps on test tubes, check the condition of the polytetrafluoroethylene (PTFE) cap liners to make sure they are clean and not deteriorated.

A4.5.1 Slowly and gently agitate test tubes to affect mixing. Mixing is complete when there is no sign of stratification. Carefully vent test tubes to release pressure. Rapid mixing will cause heating and a pressure increase with the potential for breaking the test tube. If absorbance readings exceed 1.0 or if spectrophotometric analysis is performed within 2 h, heat capped test tubes to 95°C or place in a boiling water bath for 15 + 2 min to ensure that the chemical reaction is complete. After removal, allow the test tubes to cool to room temperature.

A4.6 Standardize the spectrophotometer using distilled water at 580 nm in accordance with the instrument's operating instructions. The reagent blank (Tube 1) shall be read against distilled water. A high absorbance for the reagent indicates contamination of reagent blank or improper solution preparation. If absorbance for the reagent blank compared to distilled water is greater than 0.040 (using a 12 mm cell path length), repeat the entire standardization procedure.

A4.7 Zero the instrument using the reagent blank (Tube 1) if the absorbance is not greater than 0.040 (compared to distilled water as zero). Alternatively, the instrument may be left zeroed on distilled water, and the absorbance of the reagent blank subtracted from the absorbance of the standard solutions. Recovery shall be within ± 5 % of reagent blank.

A4.8 Read and record absorbance at 580 nm for each standard prepared (Tubes 2 through 6).

A4.9 Plot absorbance against micrograms of formaldehyde in the color developed solution. Note the amount of formaldehyde in micrograms is based upon the concentration of formaldehyde in standard Solution B, which is dependent upon

the standardization carried out on standard Solution A in Annex A3.

A4.9.1 *Example*—If standard Solution A = 100 mg/mL then standard Solution B = 10.00 µg/mL:

Tube 1 = 0 mL Standard Solution B  
 ×10.00 µg/mL = 0.00 µg total formaldehyde  
 Tube 2 = 0.10 mL Standard Solution B  
 ×10.00 µg/mL = 1.00 µg total formaldehyde  
 Tube 3 = 0.30 mL Standard Solution B  
 ×10.00 µg/mL = 3.00 µg total formaldehyde  
 Tube 4 = 0.50 mL Standard Solution B  
 ×10.00 µg/mL = 5.00 µg total formaldehyde  
 Tube 5 = 0.70 mL Standard Solution B  
 ×10.00 µg/mL = 7.00 µg total formaldehyde  
 Tube 6 = 1.00 mL Standard Solution B  
 ×10.00 µg/mL = 10.00 µg total formaldehyde

A4.9.2 The absorbance of each tube would be plotted against the total micrograms of formaldehyde in each tube.

A4.9.3 The absorbance of each chamber impinger aliquot specimen determined in 10.4.3 is compared to this calibration curve, and the total micrograms of formaldehyde in the aliquot is represented as C<sub>a</sub> in 11.2.

NOTE A4.1—The calibration curve as described in this annex is provided as an example. If absorbance readings are outside of this range, dilute the solution with distilled water to a concentration that is within the calibration curve. If absorbance readings exceed 1.0, place capped test tubes in a boiling water bath for 15 ± 2 min to ensure that the chemical reaction is completed. Vent test tubes to release pressure. Remove tubes from water bath and allow to cool to room temperature.

A4.10 Preparation of the calibration curve (A4.3-A4.9) shall be repeated at least once more and the final calibration line shall reflect the composite of the determinations (or the curve shall be calculated using a linear least squares fitting technique). The calibration curve may not be linear at high formaldehyde concentrations (high absorbance readings). If the plot in A4.9 shows the last few points deviating from linearity, omit the points from calculations or repeat entire procedure. Further, the curve should be frequently checked based on changes in reagent lot numbers, past experience, data scattering, or instrument instability.

## APPENDIX

### (Nonmandatory Information)

#### X1. REAGENTS, MATERIALS, AND EQUIPMENT FOUND SUITABLE FOR USE

##### X1.1 Air-Sampling Apparatus

NOTE X1.1—Other apparatus and instruments may be used if equivalent results are anticipated.

###### X1.1.1 Midget Impingers.<sup>12</sup>

<sup>12</sup> Ace Glass Stopper No. 7531-06 and 30-mL Bottle No. 7531-04, available from Ace Glass Inc., P.O. Box 688, Vineland NJ 08360, or Lurex No. 191-4050, available from Lurex Scientific, have been found suitable for this purpose.

###### X1.1.2 Rotameters, 1 L/min.<sup>13</sup>

X1.1.3 *Line Filter*, with desiccant (to dry the air before entering rotameters).<sup>14</sup>

###### X1.1.4 *Polytetrafluoroethylene (PTFE) Tubing*.<sup>14</sup>

###### X1.1.5 *Buret*, 250 or 500 mL (to calibrate rotameters).<sup>14</sup>

<sup>13</sup> Scott Specialty Gases, Model S2-315-2-4 with stainless steel float, available from 7425 North Oak Park Ave., Chicago, IL 60648, have been found suitable for this.

<sup>14</sup> Available from scientific supply houses.

X1.1.6 *Impinger Pumps*.<sup>14</sup>

X1.1.7 *Film-Type Laboratory Calibrators or Bubble Tube*, for calibrating pumps and rotameters.<sup>15</sup>

## X1.2 Analytical Apparatus

X1.2.1 *Spectrophotometer*.<sup>16</sup>

X1.2.2 *Spectrochek*,<sup>14</sup> for calibration of the spectrophotometer.

X1.2.3 *Beaker*, 150 mL, low form.<sup>14</sup>

X1.2.4 *Volumetric Flask*, 1000 mL.<sup>14</sup>

X1.2.5 *Volumetric Flask*, 100 mL.<sup>14</sup>

X1.2.6 *Volumetric Flasks*, two, 10 mL.<sup>14</sup>

X1.2.7 *Buret*, 25 mL, Class A.<sup>14</sup>

X1.2.8 *pH meter*.<sup>14</sup>

X1.2.9 *Magnetic Stirrer*.<sup>14</sup>

X1.2.10 *Pipet*, volumetric, 4 mL.<sup>14</sup>

X1.2.11 *Pipet*, volumetric, 50 mL, Class A.<sup>14</sup>

X1.2.12 *Pipet*, volumetric, 6 mL, Class A.<sup>14</sup>

X1.2.13 *Pipet*, long-tip Mohr type, 2 by 0.01 mL.<sup>14</sup>

X1.2.14 *Pipet, Mohr*, 10 by 0.1 mL.<sup>14</sup>

X1.2.15 *Safety Bulb*, for pipeting.<sup>14</sup>

X1.2.16 *Test Tubes*, 16 by 150 mm, with polytetrafluoroet-

hylene (PTFE) lined screw caps.<sup>14</sup>

X1.2.17 For repetitive analyses of sample solutions and for added safety, use of automatic pipeting equipment may be desirable. Use of the following have been found suitable.<sup>14</sup>

X1.2.17.1 *Brinkman Dispensers*, volume 0.1 to 0.5 mL (for chromotropic acid), volume 1 to 10 mL (for sulfuric acid), and volume to 25 mL (for distilled water).<sup>14</sup>

X1.2.17.2 *Oxford Macro-Set Pipet*.<sup>14</sup>

X1.2.17.3 *Tips*, 250, for transferring 4 mL aliquots.<sup>14</sup>

## X1.3 Reagents

X1.3.1 *Chromotropic Acid Reagent*—Dissolve 0.10 g of chromotropic acid (4,5-dihydroxy-2,7-naphthalene-disulfonic acid disodium salt) in freshly distilled water and dilute to 10 mL. This solution is to be made up daily.

X1.3.2 *Sulfuric Acid* ( $H_2SO_4$ ), concentrated, reagent grade. Nitrate concentration shall be less than 10 ppm.

X1.3.3 *Buffer Solution*, pH 9.0.

X1.3.4 *Hydrochloric Acid*, (HCl) 0.100 N, standard.

X1.3.5 *Sodium Sulfite Solution*, 1.0 M—Dissolve 12.67 g anhydrous sodium sulfite ( $Na_2SO_3$ ) (ACS assay 99.5 %) in a 100-mL volumetric flask and dilute to the mark with freshly distilled water. The correct amount to be dissolved should be 12.6/ACS assay of the anhydrous sodium sulfite actually being used (read assay from bottle label).

X1.3.6 *Formaldehyde Solution*, weight 37 %.

X1.3.7 *Sodium Bisulfite*, ( $NaHSO_3$ ), reagent grade.

X1.3.8 *Mild Liquid Soap*.

<sup>15</sup> Available from SKC Inc., 334 Valley View Rd., Eighty Four, PA 15330-9614.

<sup>16</sup> Milton Roy Spectronic 20 Spectrophotometer, available from scientific supply houses, or equivalent, has been found suitable for this purpose.

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