

Test Method for Free and Hydrolyzed Formaldehyde: Water Extraction

1. Purpose and Scope

1.1 This test method is applicable to wettable (non-hydrophobic) textile fabrics that may contain free or hydrolyzed formaldehyde, particularly fabrics finished with chemicals containing formaldehyde. It provides a water extraction process and a subsequent colorimetric analysis of the amount of free and hydrolyzed formaldehyde extracted.

2. Principle

2.1 A weighed fabric specimen is submerged in a flask filled with deionized water. The sealed or capped flask is placed in a water bath at a controlled temperature for a specified length of time. The amount of formaldehyde extracted into the water is then determined colorimetrically.

3. Terminology

3.1 **free formaldehyde**, n.—formaldehyde that is not bonded to a finish or a fabric. In this form, formaldehyde can be readily extracted from the fabric by immersion in water.

3.2 **hydrolyzed formaldehyde**, n.—although originally part of larger chemical structure, such as a crosslinking reactant, the formaldehyde is cleaved from the larger molecule and dissolved into the water.

4. Safety Precautions

NOTE: These safety precautions are for information purposes only. The precautions are ancillary to the testing procedures and are not intended to be all inclusive. It is the user's responsibility to use safe and proper techniques in handling materials in this test method. Manufacturers MUST be consulted for specific details such as material safety data sheets and other manufacturer's recommendations. All OSHA standards and rules must also be consulted and followed.

4.1 Good laboratory practice should be followed. Wear safety glasses in all laboratory areas.

4.2 When handling glacial acetic acid to prepare Nash reagent, use chemical goggles or face shield, impervious gloves and an impervious apron during preparation. Concentrated acids should be handled only in an adequately ventilated laboratory hood. CAUTION: Always add

acid to water.

4.3 Formaldehyde is a carcinogen. Use in an adequately ventilated laboratory hood. Avoid inhalation or skin contact. Use chemical goggles or face shield, impervious gloves and an impervious apron when working with formaldehyde (see 8.1 and 9.1).

4.4 An eyewash/safety shower should be located nearby and a self-contained breathing apparatus should be readily available for emergency use.

4.5 Exposure to chemicals used in this procedure must be controlled at or below levels set by governmental authorities (e.g., Occupational Safety and Health Administration's [OSHA] permissible exposure limits [PEL] as found in 29 CFR 1910.1000; see www.osha.gov for latest version). In addition, the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) comprised of time weighted averages (TLV-TWA), short term exposure limits (TLV-STEL) and ceiling limits (TLV-C) are recommended as a general guide for air contaminant exposure which should be met (see 14.3).

5. Uses and Limitations

5.1 The procedure is intended for use in the range of free and hydrolyzed formaldehyde on non-hydrophobic fabric from 20 µg/g up to about 3500 µg/g. This test method approximates hydrolyzed formaldehyde and closely simulates normal user conditions. However, TM206 is an aqueous immersion method and fabrics with a propensity for bleeding could be a concern; if the dye has an absorbance in the range of 412nm, it could interfere with the spectrophotometric measurement. It is not intended to approximate formaldehyde released under hot storage conditions.

5.2 Alternatively, AATCC TM112, Test Method for Formaldehyde Release from Fabric: Sealed Jar (see 14.1), determines free and hydrolyzed formaldehyde and additional formaldehyde as generated under more severe conditions than this test method. The appropriate test should be chosen based on that distinction (see 14.2).

6. Apparatus, Reagents, Materials

6.1 250-mL Erlenmeyer flasks with stoppers.

6.2 Weighing balance, with a minimum

sensitivity of 0.01 g.

6.3 Thermostatically controlled water bath: 40 ± 1°C (105 ± 2°F).

6.4 Nash reagent prepared from ammonium acetate, acetic acid and acetylacetone and water (see 7.1).

6.5 Formaldehyde solution, approximately 37% (see 4.3).

6.6 Volumetric flasks, 50, 250, 500 and 1000-mL, Class A.

6.7 Volumetric pipettes, 1, 2, 3, 5, 10, 15, 20, 25, 30 and 100-mL, all calibrated "to deliver" and meeting Class A volume accuracy and flow time requirements, or a digital, variable-volume pipette capable of meeting Class A requirements.

6.8 A 1-L clean brown glass bottle.

6.9 Spectrophotometer, capable of reading absorbance to a minimum of three decimal places, at a wavelength of 412 nm.

6.10 Test tubes (see 14.4).

6.11 Distilled or deionized water. Hereafter, referred to as deionized water.

6.12 pH meter, calibrated and accurate to 0.01

7. Preparation of Nash Reagent

7.1 Nash Reagent: In a 1000-mL volumetric flask, dissolve 150 g of ammonium acetate in 800-mL of deionized water; add 3.0 ± 0.1 mL of glacial acetic acid and 2.0 ± 0.1 mL of acetylacetone. Add deionized water up to the 1000-mL level and mix. Store in a capped brown bottle.

7.1.1 Newly made Nash Reagent requires a 12 h wait period before being used as the reagent darkens slightly in color during that time period. The reagent may be used up to 8 weeks after it is made. However, since the sensitivity may change slightly over a long period of time, it is good practice to run a calibration curve weekly or when used to correct for the slight changes in the standard curve.

8. Preparation of Standard Solution and Calibration

8.1 Prepare a 1500 µg/mL stock solution of formaldehyde by diluting 3.8-mL of reagent grade formaldehyde solution (approximately 37%, see 4.3) to 1.0-L with deionized water in a volumetric flask. Equilibrate the stock solution for a minimum of 24 h in a capped/stoppered flask before standardization. Determine the concentration of formaldehyde in the

stock solution by a standard method (see Section 9. Standardization of Stock Formaldehyde Solution, or any other suitable procedure such as sodium sulfite titration using 0.1 *N* HCl (see 14.5). Record the actual concentration of this standardized stock solution. This stock solution will keep for at least four weeks and is used to prepare standard dilutions.

8.1.1 A 1:10 dilution of the standardized formaldehyde stock solution is prepared by pipetting 25-mL of the standardized stock solution into a 250-mL volumetric flask and diluting to the mark with deionized water. The stock solution is then titrated and its concentration is determined as $\mu\text{g/mL}$.

8.2 A 5-concentration calibration curve, which may include zero, is suggested. Prepare the calibration curve by pipetting from the following: 0, 1, 3, 5, 10, 15, 20 and 30-mL volumes of the 1:10 dilution into 500-mL volumetric flasks then adding deionized water to the 500-mL level. (If, for example, the standardized stock solution were found to be 1470 $\mu\text{g/mL}$ by titration, calculate new values for the calibration curve abscissa; i.e., 0.0, 0.29, 0.88, 1.47, 2.94, 4.41, 5.88, 8.82 $\mu\text{g/mL}$ using regression analysis.)

8.2.1 When 1, 3, 5, 10, 15, 20 and 30-mL aliquots of the 1:10 dilution of the standardized stock solution from 8.1 are diluted with deionized water in 500-mL volumetric flasks, formaldehyde solutions containing approximately 0.30, 0.90, 1.5, 3.0, 4.5, 6.0 and 9.0 $\mu\text{g/mL}$ formaldehyde respectively will be obtained. Record the calculated concentration of each solution as determined by section 9 Standardization of Stock Formaldehyde. The equivalent concentrations of the formaldehyde in the test fabric based on the weight of accurately known 1 g of the test fabric and 100-mL of water in the Erlenmeyer flasks will be 100 times the accurate concentrations of these standard solutions.

8.3 Use 5 mL aliquots of each of the standard solutions and the procedure described in 11.4-11.7 to prepare a calibration chart in which $\mu\text{g/mL}$ formaldehyde are plotted against absorbance.

9. Standardization of Formaldehyde Stock Solution

9.1 The stock solution containing approximately 1500 $\mu\text{g/mL}$ of formaldehyde must be standardized in order to produce precise calculations from the calibration curve required in colorimetric analysis.

9.2 An aliquot of the stock solution is reacted with an excess of sodium sulfite followed by a back-titration with standard acid solution to a pH of 9.5.

9.2.1 Apparatus: 10 mL-volumetric pipette, 50-mL volumetric pipette, 50-mL

burette, 150-mL beaker.

9.2.2 Reagents: 1.0 *M* sodium sulfite (126 g Anhydrous $\text{Na}_2\text{SO}_3/\text{L}$), 0.02 *N* sulfuric acid (can be purchased in standardized form from chemical supply companies or must be standardized from standard NaOH solution). Do not use commercial standardized sulfuric acid that has been stabilized with formaldehyde. If there is a doubt, check with the chemical supplier.

9.2.3 Procedure:

A. Pipette 50-mL of the 1.0 *M* sodium sulfite (Na_2SO_3) into the beaker.

B. Pipette 10-mL of the stock formaldehyde solution to a beaker.

C. Titrate the solution with the standard 0.02 *N* H_2SO_4 to an endpoint of pH of 9.5.

9.2.4 Record the volume of acid used to the nearest 0.01-mL. (The volume of acid should be approximately 25-mL for 0.02 *N* acid.)

Calculations:

$$C = (30,030) (A) (N)/10$$

where:

C = Wt/Vol concentration of formaldehyde ($\mu\text{g/mL}$)

A = Vol of acid used (mL)

N = Normality of acid

9.3 Repeat the titration standardization in duplicate or triplicate. Average the results.

9.4 Use the determined concentration in preparing the calibration curve for the colorimetric analysis.

10. Test Specimens

10.1 Samples should immediately be placed into separate zipper-type closure plastic bags when sampled. As an extra precaution for maintaining their original state the samples may be wrapped in aluminum foil before being placed in the plastic bags.

10.2 Cut approximately 1-g specimens; weigh each one to ± 0.01 g. Perform in duplicate for each sample. If there is a delay in testing the 1-g specimens once they are cut, they should be put back into the zipper-type closure plastic bags (and re-wrapped in foil if previously done) until testing commences.

11. Procedures

11.1 Pipette 100.0-mL of deionized water into each Erlenmeyer flask. Place a fabric specimen in each flask. The fabric should be completely submerged in the water and not float on the surface (see 14.6). A stirring rod may be used to push and keep the fabric below the water surface. Cap the flasks and place them in the water bath at $40 \pm 1^\circ\text{C}$ ($105 \pm 2^\circ\text{F}$) for 60 ± 2 min. Shake the flasks every 5 min by

hand or use an ultrasonic water bath for agitation. If using an ultrasonic bath, check the water frequently for temperature changes.

11.2 Remove the flasks from the water bath.

11.3 Remove the fabric from the flasks. Recap the flasks and shake them to mix any condensation formed on the sides. Allow solutions to cool for 30 min.

11.4 Pipette 5-mL of Nash reagent into a suitable number of test tubes, small (50-mL) Erlenmeyer flasks, or other suitable flasks (colorimeter or spectrophotometer tubes can be used directly, see 14.4) and pipette 5-mL of the reagent into at least one additional tube for a reagent blank. Add 5-mL aliquots from each of the sample incubation jars to the tubes. Reagent blanks are prepared by adding 5-mL of the Nash reagent and 5-mL of deionized water to the tubes.

11.5 Mix and place the tubes in a $40 \pm 1^\circ\text{C}$ ($105 \pm 2^\circ\text{F}$) water bath for 30 ± 1 min. Remove tubes from bath. Cap with stoppers or plastic paraffin film and allow to cool to room temperature away from direct light.

11.6 Read the absorbance in the spectrophotometer against the reagent blank at 412 nm. **Caution:** Exposure of the developed yellow color to direct sunlight for a period of time will cause some fading. If there is appreciable delay in reading the tubes after color development and strong sunlight is present, care should be exercised to protect the tubes from light. Otherwise the color is stable for considerable time (at least overnight) and reading may be delayed (see 14.7 and 14.8).

11.7 Determine the $\mu\text{g/mL}$ formaldehyde (HCHO) in the sample solutions using the prepared calibration curve (see 8.3 and 14.9).

12. Calculations and Report

12.1 Calculate the amount of formaldehyde released for each specimen to the nearest $\mu\text{g/g}$ using the following equation:

$$F = (C) (100)/W$$

where:

F = concentration of formaldehyde ($\mu\text{g/g}$),

C = concentration of formaldehyde in solution as read from the calibration curve

W = weight of the test specimen, g.

12.2 If performing both this test and AATCC TM112, care should be used in reporting calculated results as this test uses 100-mL of water and AATCC TM112 uses 50-mL.

13. Precision and Bias

13.1 Precision.

13.1.1 Interlaboratory tests. One inter-