



Designation: D 5014 – 94 (Reapproved 2000)^{ε1}

Standard Test Method for Measurement of Formaldehyde in Indoor Air (Passive Sampler Methodology)¹

This standard is issued under the fixed designation D 5014; 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 (ε) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Editorial corrections were made throughout in March 2000.

1. Scope

1.1 This test method covers personal or area measurements of formaldehyde in indoor air in the range from 0.01 to 17 mg/m³ (0.008 to 14 ppm v/v). Formaldehyde is collected in a passive diffusion sampler, and analyzed by a colorimetric method using 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH). The recommended sampling time is 15 min to 24 h.

1.2 The lower quantification limit of the MBTH test method is 0.03 µg of formaldehyde per millilitre of absorbing solution used. A formaldehyde concentration of 0.01 mg/m³ (0.008 ppm v/v) can be determined in indoor air, based on using an aliquot of 5 mL of absorbing solution in the prescribed sampler for a period of 24 h and observing a minimum difference of 0.05 absorbance units from the blank when using spectrophotometer cells of path length 1 cm.

1.3 Water soluble aliphatic aldehydes give a significant positive interference (**1**, **2**)² nearly equal to formaldehyde on a molar basis. Further information on estimating potential and actual interferences from aliphatic aldehydes may be found in 6.2 and 10.1.7. Most other compounds which react to produce colored products are not gaseous or water soluble and, consequently, should not interfere.

1.4 The values stated in SI units are to be regarded as the standard.

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.* Specific precautionary statements are given in 8.3 and 8.4.

¹ This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

Current edition approved June 15, 1994. Published August 1994. Originally published as D 5014 – 89. Last previous edition D 5014 – 89.

² The boldface numbers in parentheses refer to the references at the end of this test method.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water³

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres⁴

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere⁴

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): (The Modern Metric System)⁵

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D 1356. For an explanation of units, symbols, and conversion factors, refer to IEEE/ASTM SI 10.

3.2 Descriptions of Terms:

3.2.1 *Knudsen disk*—a gas-permeable diffusion disk which regulates the transfer of gas by the principles of Knudsen diffusion. Details concerning the construction of a Knudsen disk are described in 7.1.2.

4. Summary of Test Method

4.1 Formaldehyde is absorbed into a 0.05 % aqueous solution of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) contained in a sampler consisting of a glass vial with a septum cap that retains a Knudsen disk. During air sampling the vial is inverted to establish contact between the absorbing liquid and the Knudsen disk. Formaldehyde passes from the ambient atmosphere into the MBTH solution through the Knudsen disk at a constant rate. After collection, the resulting azine is oxidized by a ferric chloride-sulfamic acid solution to form a blue cationic dye in acidic medium. The concentration of the blue cation is measured by colorimetry at 628 nm (**1**, **3-5**). The air concentration of formaldehyde is computed from

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.03.

⁵ *Annual Book of ASTM Standards*, Vol. 14.03.

the amount of formaldehyde collected divided by the product of the diffusion rate and the time of exposure.

4.2 The mechanism of the present procedure as applied to formaldehyde includes the following steps: reaction of formaldehyde with 3-methyl-2-benzothiazolinone hydrazone hydrochloride, forming the azine which is oxidized to a reactive cation, and formation of the blue cation (1, 3).

5. Significance and Use

5.1 This test method allows field measurement of formaldehyde in indoor air at concentrations from 0.01 to 17 mg/m³ (0.008 to 14 ppm) using sampling times between 15 min and 24 h. A 24-h sampling time is recommended to measure time-weighted average formaldehyde concentrations over the range from 0.01 to 0.2 mg/m³ (0.008 to 0.16 ppm v/v) in offices and residences. An 8-h sampling time allows measurement over the range of 0.03 to 0.6 mg/m³ (0.025 to 0.5 ppm v/v). The test method is suitable for both area or personal monitoring.

5.2 This test method allows sampling and quantification of formaldehyde under field conditions with the aid of a portable field colorimeter, without the need for any laboratory support.

6. Interferences

6.1 The following classes of compounds react with MBTH to produce colored products (1, 5). These are aromatic amines, imino heterocyclics, carbazoles, azo dyes, stilbenes, Schiff bases, the aliphatic aldehyde 2,4-dinitrophenylhydrazones, and compounds containing the p-hydroxy styryl group. Most of these compounds are not gaseous or water soluble and, consequently, should not interfere with the analysis of formaldehyde in the atmosphere.

6.2 Aliphatic aldehydes give a positive response with the MBTH method equal to 75 % or less that of formaldehyde on a molar basis (1). The Knudsen disk discriminates against aldehydes having molecular weights greater than formaldehyde in proportion to the ratio of the square roots of their molecular weights.⁶ See 10.1.7 for discussion of a method for confirming whether or not a positive interference exists in the event that other aldehydes are known or suspected to be present.

6.3 Effect of Storage:

6.3.1 Formaldehyde is fairly stable in 0.05 % MBTH since only approximately 5 % of the formaldehyde is lost after standing in the MBTH for 13 days (1).

6.3.2 Formaldehyde samples stored in the samplers with a solid cap are stable for at least one week at room temperature when stored in the dark. After one week the MBTH solution darkens and a precipitate begins to form. Exposure to elevated temperatures reduces the stability of samples. In one experiment samples stored at 313 K (105°F) darkened noticeably after 24 h (6).

7. Apparatus

7.1 *Passive Air Sampler*—An example of the sampler is shown in Fig. 1. It consists of a cylindrical glass vial 70 mm high by 20.5 mm diameter, with a 20–400 thread finish having



FIG. 1 Passive Sampler Showing Vial, Septum Cap Retaining Knudsen Disk, and Clip for Affixing Sampler for Personal or Area Samples

an opening 13.9 mm (³⁵/₆₄ in.) in diameter. Mated to the vial is a septum cap with an opening equal in diameter to that of the vial. The septum cap retains a Knudsen disk of diameter 17.5 mm (¹¹/₁₆ in.). Before and after sampling, the septum cap is replaced with a solid cap lined with polyethylene or polytetrafluoroethylene. A “pencil” style clip is slipped over the vial to allow it to be affixed to clothing or other support for collecting a personal or area sample, respectively.⁷

7.1.1 Vials with other thread finishes or septum caps with a different opening size may be used; however, the sampling rate shall be redetermined. When the alternative septum cap and vial having openings of equal size, the new sampling rate may be computed from the relative ratio of opening sizes as follows:

$$SR_{\text{new}} = SR \times (A_{\text{new}}/A) \quad (1)$$

where:

⁷ The passive sampling device used in the development and performance evaluation of this test method was manufactured by Solutions Environmental Health, 6687 N. Blackstone Ave., Fresno, CA 93710–3524, which is the sole source of supply of the sampler known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹ which you may attend.

⁶ Supporting data are available from ASTM Headquarters. Request RR:D-22.05-02.



- SR_{new} = sampling rate of new vial-septum cap configuration,
 SR = sampling rate of Knudsen disk in specified vial-septum cap configuration,
 A_{new} = area of new vial-septum cap opening, and
 A = area of specified vial-septum cap configuration (1.52 cm²).

When the septum cap and the vial have different opening sizes, the new sampling rate shall be experimentally determined in accordance with 10.3.

7.1.2 *Knudsen Disk*⁸—The Knudsen disk consists of porous polytetrafluoroethylene membranes of 0.07 mm thickness and 0.02 µm pore sizes thermally bound in such a manner as to preserve their microporous properties to both sides of a 1.6-mm (1/16-in.) thick core of macroporous high-density polyethylene. Using the prescribed sampler, the Knudsen disk allows the ambient atmosphere to be sampled for formaldehyde at a constant rate of approximately 11.6 mL/min independent of drafts over the range from 0.13 to 1.3 m/s (25 to 250 ft/min). The sampling rate normally is provided by the supplier of the Knudsen disks, but may also be determined experimentally in accordance with 10.3.

7.2 *Spectrophotometer*, an instrument capable of measuring accurately the developed color at the narrow absorption band of 628 nm. Portable colorimeters with a sample well that accepts the vial are available (6, 7), and allow the analysis procedure to be carried out in the field. The sensitivity is increased by a factor of two because the measured path length through the color-developed solution is approximately doubled relative to a 1-cm spectrophotometer cell.

7.3 *Standard pH Meter*.

7.4 *Magnetic Stirrer*.

7.5 *Erlenmeyer Flask*, 125 mL.

7.6 *Capped Analysis Vials*, glass vials able to hold 6 mL conveniently, having closures lined with polyethylene or foil. Avoid closures lined with paper or tetrafluoroethylene.

8. Reagents

8.1 *Purity of Reagents*—Unless otherwise stated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁹ Other grades may be used, provided it is ascertained that use of the reagent does not lessen the accuracy of the test method.

⁸ The Knudsen diffusion disk used in this test method is covered by a patent held by Robert R. Miksch, Ph.D., 548 E. Mallard Circle, Fresno, CA 93720-1227. Interested parties are invited to submit information regarding the identification of acceptable alternatives to this patented item to the Committee on Standards, ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.

⁹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.2 *Purity of Water*—References to distilled water shall be understood to mean distilled water, which is Type II reagent water conforming to Specification D 1193.

8.3 *3-Methyl-2-Benzothiazolinone Hydrazone Hydrochloride Absorbing Solution (MTBH)* (0.05 %)—Dissolve 0.5 g of MBTH in distilled water and dilute to 1 L. This colorless solution can be filtered by gravity, if slightly turbid, and is stable for a least one week, after which it becomes pale yellow. Stability may be increased by storing the solution in a dark bottle under refrigerated conditions. Alternatively, MBTH reagent tablets are commercially available, premeasured so that one tablet dissolved in 5 mL of distilled water provides a 0.05 % solution. (6) (**Warning**—Mild irritant. Avoid contact with skin and eyes. Wash with water.)

8.4 *Oxidizing Reagent*—Dissolve 1.6 g of sulfamic acid and 1.0 g of ferric chloride hexahydrate in distilled water and dilute to 100 mL. (**Warning**—Caustic. Avoid contact with skin and eyes. Wash with water.)

8.5 *Formaldehyde Standard Solution “A”* (1 mg/mL)—Dilute 2.7 mL of 37 % formalin solution to 1 L with distilled water. This solution must be standardized as described in Section 9. This solution is stable for one year, after which it should be restandardized.

8.6 *Formaldehyde Standard Solution “B”* (10 µg/mL)—Dilute 1 mL of “A” to 100 mL with 0.05 % MBTH solution. Prepare fresh daily.

8.7 *Sodium Sulfite* (2 N)—Dissolve 31.5 g of anhydrous sodium sulfite in distilled water to 250 mL. Prepare fresh daily.

8.8 *Hydrochloric Acid, Standard Solution* (0.05 N)—Dilute 4.28 mL of concentrated hydrochloric acid (HCl, specific gravity 1.19) to 1 L.

9. Calibration and Standardization

9.1 *Standardization of Formaldehyde Standard Solution “A”*:

9.1.1 Place 50 mL of 2 N sodium sulfite in a 125-mL Erlenmeyer flask. Stir the solution using a magnetic stirrer.

9.1.2 Measure and accurately record the pH. It should be around 10.

9.1.3 Add 25 mL of formaldehyde standard solution “A.” The pH should rise sharply to about 12.

9.1.4 Using the pH meter as a continuous monitor, titrate the solution back to its exact original pH using 0.05 N hydrochloric acid. Approximately 17 mL will be required.

9.1.5 One mL of 0.05 N hydrochloric acid is equivalent to 1.50 mg of formaldehyde. Therefore, since 25 mL of formaldehyde standard solution “A” was titrated, the millilitres of 0.05 N acid used in the titration multiplied by 0.060 equals the formaldehyde concentration of the standard solution in milligrams per millilitre. When stored in a brown glass bottle, formaldehyde standard solution “A” should be recalibrated on a quarterly basis.

9.2 *Preparation of Standard Curve*:

9.2.1 Pipet 0, 0.5, 1.0, 3.0, 5.0, and 7.0 mL of standard formaldehyde solution “B” into 100 mL volumetric flasks. Dilute to volume with 0.05 % MBTH solution. The solutions contain 0, 0.05, 0.1, 0.3, 0.5, and 0.7 micrograms of formaldehyde per millilitre.

9.2.2 After final dilution, let standards stand for 1 h.