



Designation: D 6303 – 98

Standard Test Method for Formaldehyde in Water¹

This standard is issued under the fixed designation D 6303; 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.

1. Scope

1.1 This test method covers the determination of the formaldehyde monomer concentration in water and wastewater.

1.2 This test method is suitable for free formaldehyde concentrations in the range of 0.2 to 7.0 mg/L. For samples containing concentrations greater than 7 mg/L, dilute with reagent water prior to analysis. Samples containing between 0.02 and 0.5 mg/L may be run using a 10-cm cell.

1.3 This test method is for use with reagent water and wastewater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 Formaldehyde polymers react partially or slowly, or both, making this test method unsuitable for analysis of these compounds.

1.5 For specific hazards statements, see Section 9. *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:²

D 1129 Terminology Relating to Water

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits

D 1193 Specification for Reagent Water

D 1293 Test Methods for pH of Water

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water

D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data

D 4453 Practice for Handling of Ultra-Pure Water Samples

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *formaldehyde, n*—a monomeric formaldehyde that is unbound.

3.2.1.1 *Discussion*—This may include dimers, polymers, and formaldehyde resins, which are easily broken down. It generally does not include the firmly bound formaldehydes that are integral to complex structures, such as wood resins, etc. Since bound formaldehyde is not necessarily quantitatively released and judgement is needed to determine the necessity and extent of releasing it, bound formaldehyde is considered to be outside the scope of this test method.

4. Summary of Test Method

4.1 An aliquot of the sample containing 0.2 to 7 mg/L of formaldehyde is combined with an equal volume of the acetylacetone reagent in a test tube. The tube is capped, shaken, and reacted at 60°C for 10 min. After cooling, the absorbance of the solution is read at 412 nm. Colored or turbid samples are extracted with *n*-butanol prior to reading the absorbance, and the reading then is taken on the *n*-butanol extract. Concentration is calculated from a curve of standard formaldehyde solutions.

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.



4.2 The chemical reaction is based on the Hantzsch reaction.³ Formaldehyde reacts with acetylacetone in the presence of ammonium ion to form the yellow compound, 3,5-diacetyl-1,4-dihydro-lutidine.

5. Significance and Use

5.1 This test method is used to determine the concentration of formaldehyde monomer present in water, avoiding many of the problems associated with other methods. The equipment required is fairly simple, so the test can be performed under field conditions. Because of the near-neutral pH of the reagents, the mild reaction conditions result in very little degradation or formation of free formaldehyde. The reagents are not affected by nitrates or reducing agents.

6. Interferences

6.1 Color or turbidity after the reaction may interfere in some samples. The butanol extraction described in the procedure removes the lutidine yellow color from these interferences.

6.2 Acetaldehyde gives rise to diacetyldihydro-collidine that has an absorption peak at 388 nm and will overlap the diacetyldihydro-lutidine. Ethylene glycol forms formaldehyde under these reaction conditions. Amines can compete with the reaction, causing negative interferences. Periodate destroys the color, but this destruction can be prevented by additions of iodine and thiosulfate.³

6.3 Formaldehyde polymers, except paraformaldehyde, give very little interferences.

6.4 Phenols, sulfites, and other reactive substances combine with free formaldehyde to form other compounds.

7. Apparatus

7.1 *Photometer*—A spectrophotometer or filter photometer, suitable for use at 412 nm.

NOTE 1—Filter photometers and photometric practices prescribed in this test method shall conform to Practice E 60. Spectrophotometers and absorption cells shall conform to Practice E 275.

7.2 *Absorption Cells* (see Note 1)—Normally cells have a path length of 1 cm for this test method. Longer paths may be used to improve the sensitivity for concentrations below 0.2 mg/L.

7.3 *Heating Block*, or water bath, for test tubes that can be regulated to $60^{\circ} \pm 3^{\circ}\text{C}$.

7.4 *Borosilicate Test Tubes*, TFE-fluorocarbon-lined screw caps. A recommended size is 5- to 10-mL.

7.5 *Centrifuge*, with capped tubes.

7.6 *Buret*, 50-mL

7.7 *Magnetic Stirrer*, and stir bars.

7.8 *pH Meter*, conforming to the requirements of Test Method D 1293.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used for all tests. Unless otherwise indicated, it is intended that

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided that it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*— Unless otherwise indicated, references to water used shall be understood to mean reagent water conforming to Type II of Specification D 1193, or better. Water for this test method shall be free of formaldehyde, residual chlorine, phenolic compounds, and substances that interfere with this test method.

NOTE 2—Because formaldehyde is so ubiquitous, care must be taken to prevent its contamination into the water. Glassware and exposure to air act as sources of contamination. The water must be checked to be sure it is clean enough before running the analysis. If it is not clean enough, another source must be found, or clean-up procedures must be instituted. Boiling reagent water and cooling to room temperature under an inert gas purge has been found to be quite effective. Another technique is to distill from permanganate in a formaldehyde free atmosphere.

NOTE 3—Charcoal filters used on some water purification systems have been packed with a preservative formaldehyde.

8.3 *Acetylacetone Reagent*—Weigh 154 g of ammonium acetate into a 400-mL beaker. Dissolve the crystals in a small volume of water. Transfer the solution quantitatively to a 1-L volumetric flask. Add 2.0 mL of acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$, also known as 2,4-pentanedione) and 3.0 mL of glacial acetic acid (sp. gr. 1.05) to the flask. Add enough water to mix thoroughly, and dilute to 1 L. Store the solution in a brown glass container at 4°C . This reagent will last for more than three months if properly stored.

8.4 *Acetic Acid*, glacial (sp. gr. 1.05)-aldehyde-free.

8.5 *n-Butanol* (optional)—for colored or turbid samples.

8.6 *Formaldehyde Solution Stock* (1000 mg/L)—Dilute 2.7 mL of commercially available 37 % formaldehyde solution to 1 L with water. Standardize using the procedure described in 8.6.1. The solution should be stored at room temperature, in the dark, and should be standardized every six months. The solution appears to be stable indefinitely.

8.6.1 *Standardization of the Stock Solution*:

8.6.1.1 Calibrate pH meter with the standard 7.0 and 10.0 pH buffers.

8.6.1.2 Pipet 20.0 mL of sodium sulfite solution into a 125-mL Erlenmeyer flask, and add approximately 30 mL water to cover the stir bar and pH probe.

8.6.1.3 Add a magnetic stir bar, and place solution on magnetic stirrer.

8.6.1.4 Measure and record the pH while stirring.

NOTE 4—The pH should be near 9.5.

8.6.1.5 Add a 50.0-mL aliquot of the formaldehyde stock solution. Cap, mix, and allow to stand for 5 min.

³ Nash, T., "The Calorimetric Estimation of Formaldehyde by Means of the Hantzsch Reaction," *Biochemistry*, 55, 1953, p. 416.

⁴ *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 *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*. U.S. Pharmaceutical Convention, Inc. (USPC) Rockville, MD.