Designation: D 6303 – 98

An American National Standard

Standard Test Method for Formaldehyde in Water[1]

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:*

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 1293 Test Methods for pH of Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]

D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]

D 4453 Practice for Handling of Ultra-Pure Water Samples[2]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[3]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers[5]

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.

4.2 The chemical reaction is based on the Hantzsch reaction.[6] Formaldehyde reacts with acetylacetone in the presence of ammonium ion to form the yellow compound, 3,5-diacetyl-1,4-dihydro-lutidine.

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[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] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 15.05.

[5] *Annual Book of ASTM Standards*, Vol 03.06.

[6] Nash, T., "The Calorimetric Estimation of Formaldehyde by Means of the Hantzch Reaction," *Biochemistry*, 55, 1953, p. 416.

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.[6]

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° ± 3°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.[7] 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 ($C_5H_8O_2$, 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.

[7] *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. Pharmaceutical Convention, Inc. (USPC) Rockville, MD.

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

8.6.1.6 While stirring, titrate this mixture back to the original pH in 8.6.1.4, using 0.1 N HCl.

8.6.1.7 Calculate the concentration of the formaldehyde stock solution as follows:

$$\text{HCHO mg/mL} = \frac{(\text{HCl titrant, mL}) \times (\text{HCL, } N) \times (30.03)}{(\text{stock formaldehyde, mL})} \quad (1)$$

8.6.1.8 Perform three replications and calculate the mean concentration. Replicates should agree to within 0.3 %.

8.7 *Formaldehyde Solution, Standard (10.0 mg/L)*—Dilute 1.00 mL of the formaldehyde stock solution to 100 mL with water. Prepare fresh daily.

8.8 *Hydrochloric Acid (1.0 N)*—Prepare as directed in Practice E 200.

8.9 *Hydrochloric Acid (0.1 N), Standardized Solution*—Prepare and standardize as directed in Practice E 200.

8.10 *Sodium Sulfite Solution (1.0 M), Freshly Prepared*—Dissolve 31.5 g of anhydrous sodium sulfite in 150 mL of water, and dilute to volume in a 250-mL volumetric flask. Adjust to pH 9.5 with the 1 *N* hydrochloric acid (only a few drops).

9. Hazards

9.1 **Warning:** Glacial acetic acid can produce skin burns and severely injure the eyes. It is also combustible.

9.2 **Warning:** Acetylacetone is a mild irritant to the skin and mucous membranes.

9.3 **Warning:** *n*-Butanol is a skin and eye irritant and is flammable. **Precaution:** It also may cause inhalation irritation and should be handled in a hood.

9.4 **Warning:** Formaldehyde is a severe irritant to skin, eyes, and mucous membranes and can cause severe hypersensitivity. It also may be a potential carcinogen. It is a moderate fire hazard. **Precaution:** Protection should be taken to avoid inhalation of the vapors and skin contact.

10. Sampling

10.1 Collect the sample in accordance with Specification D 1192 and Practices D 3370 and D 4453.

10.2 Samples should be collected in amber glass bottles with TFE-fluorocarbon caps. If amber bottles are not available, the samples shall be protected from light. Lids containing a formaldehyde resin should not be used. The containers must be washed properly, rinsed with ethanol, and dried at 130°C for several hours before use to minimize contamination.

10.3 Sampling equipment shall be free of vinyl and other contaminating material.

10.4 Samples must be iced or refrigerated to less than 4°C from the time of collection until analysis. Exposure to light should be avoided.

10.5 Many samples are likely to be biologically active and the stability may vary for each matrix. The samples should be analyzed, as soon as possible after collection, with second-day analysis allowed only in cases where transportation makes earlier testing impractical.

11. Calibration

11.1 *Standard Curve Preparation*:

11.1.1 Prepare a series of at least three standards, encompassing the sample, by adding the specified aliquots of the standard solution (see 8.7) and water to the test tubes (volumes given are for a 2-mL standard):

Concentration, mg/L[A]	mL of Standard, 10.0 mg/L	mL of Water
0	0	2.0
0.50	0.1	1.9
1.50	0.3	1.7
2.50	0.5	1.5
3.50	0.7	1.3
4.50	0.9	1.1
6.00	1.2	0.8
7.50	1.5	0.5

[A] Actual concentration will depend on the calibration of the stock solution. These calculations assume a stock solution of 1000 mg/L.

11.1.2 Add a volume of the acetylacetone reagent, which is equal to the volume of standard to each tube. A volume of 2 mL for each is recommended. Cap tightly, shake well, and place the tubes in a heating block at 60°C for 10 ± 1 min. Remove tubes from the block and cool to room temperature.

NOTE 5—Volumes of much less than 2 mL increase the relative error of evaporation, aliquoting, etc. Sufficient quantities also are needed to rinse out the spectrophotometer cells. Too much volume may not allow sufficient time for the sample to properly warm.

11.1.3 Zero the spectrophotometer with water. Measure the absorbance of the standard solutions compared to that of water at 412 nm in a 1-cm cell. Low level samples and standards may require a longer cell to achieve the desired sensitivity. The color is stable for several hours. Fig. 1 shows several standard curves run in an aqueous solution and one curve in butanol using a 1-cm cell.

12. Procedure

12.1 All glassware and reagents must be tested routinely to demonstrate that they are free of formaldehyde contamination at a level that will not significantly affect the analysis. This testing can be done by running a blank through the analysis before samples are run. If significant contamination is found, clean-up procedures should be implemented.

12.1.1 Clean all glassware, as soon as possible after using, by rinsing with the last solvent used. This should be followed by detergent washing with hot water and rinsing with hot (tap) water, followed by a water rinse. The glassware should be drained dry. The glassware then should be heated in a 130°C oven for several hours. After cooling, store the glassware in a clean environment.

12.1.2 If contamination is a problem in reagents and solvents, higher purity materials may be needed. Solvent may be purified by distilling in an all-glass still.

12.2 For samples in the range of 0.2 to 7.0 mg/L, proceed to 12.3. If samples are known to be above this range, a dilution should be made to achieve a concentration within this range. For samples in the range 0.02 to 0.05 mg/L, the volumes of reagents and sample should be increased to 20 mL for each. This will yield sufficient volume to measure the absorbance in a 10-cm cell.

12.3 Pipet an aliquot of each sample, or diluted sample, into a screw-capped test tube. Process samples in the same manner

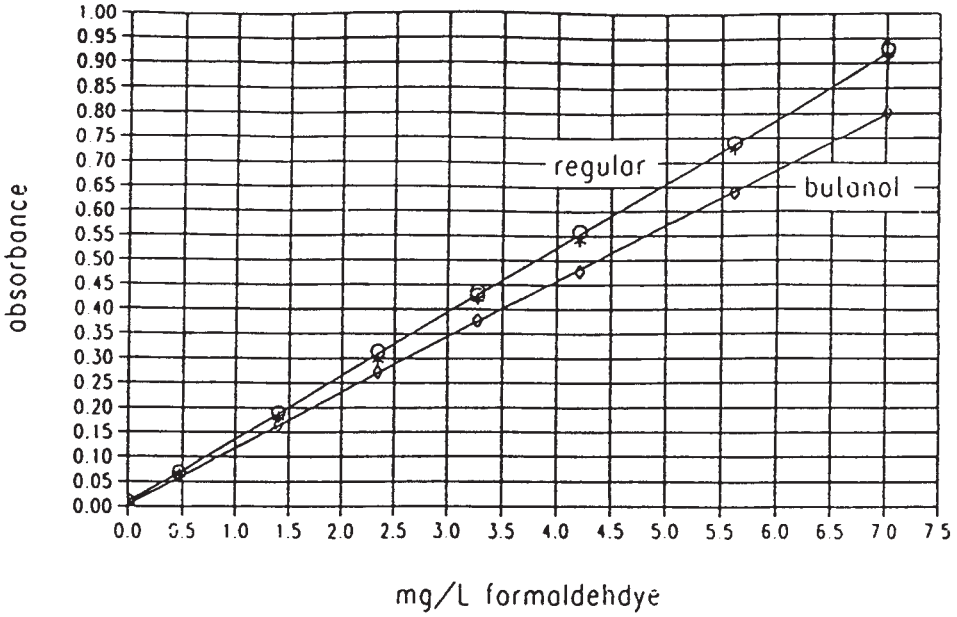

FIG. 1 Regular Versus Butanol Standards for Formaldehyde

as the standards as described in 11.1.2 and 11.1.3, using a volume of acetylacetone reagent which is equal to the volume of sample used.

12.4 If samples are colored or become turbid, or both, following the reaction, add a volume of *n*-butanol to the test tube that is equal to that of the sample plus the reagent. That is, if 2 mL of sample and 2 mL of reagent are used, add 4 mL of *n*-butanol. Swirl the tube to mix, and transfer the contents to a capped centrifuge tube. Shake the tube for 30s, and centrifuge it for 10 min. Analyze the upper *n*-butanol layer in the manner described in 11.1.3. It may be desirable to analyze the standards in the same manner, as there is a slight loss of color in the extraction process. This loss is proportionately the same for all standards, so the linearity remains.

NOTE 6—Analyst may want to re-zero the spectrophotometer with n-butanol.

13. Calculation

13.1 Calculate the formaldehyde concentration of the samples by reading the milligrams per litre on the standard curve, which corresponds to the absorbance of the sample. If a dilution factor is used, the original concentration can be calculated in the following manner:

$$\text{HCHO, mg/L} = \text{mg/L. calculated} \times V/A \quad (2)$$

where:
V = final dilution volume, mL/L, and
A = aliquot used for dilution, mL/L.

14. Report

14.1 Report results as: "Freed Formaldehyde = _____ mg/L."

15. Precision and Bias [8]

15.1 This test method was tested by twelve laboratories using reagent water. The study was restricted to reagent water because of the highly reactive and unstable nature of the material tested. The desire was to develop data demonstrating the ability of the method without the confounding alteration of the spiked analyte by unknown matrices. The results of this collaborative study may not be typical of results for matrices other than those studied.

15.2 The precision and bias for this test method were conducted using a Youden pair design and conform to Practice D 2777 and meets existing requirements for interlaboratory studies of Committee D-19 test methods.

15.3 The single-operator precision and overall precision and bias of this test method are given in Table 1. Although precision, *S*, increases with concentration, the relationship is not linear. Variation in cell path length, as allowed in this test method, will give variation in the precision.

15.4 Spectrophotometric cell path lengths used in the study for measuring the concentrations of 0.8 mg/L and higher were 1 cm in length. The lowest two concentrations were done with 5- and 10-cm cells. Cells path lengths other than those used in the collaborative study can affect the precision and may be different from that presented in Table 1.

15.5 The material tested was a purchased commercial formaldehyde solution in water. The material was available readily only in a 4000-mg/L concentration. Test concentrates were created by diluting the original solution to concentrations that were 100 times those noted in Table 1. These dilutions were

[8] Supporting data for the precision and bias statements have been filed at ASTM Headquarters.

TABLE 1 Formaldehyde

Number of Retained Values	Expected Amount in mg/L	Measured Amount in mg/L, $\bar{x}$	Overall S_T, *in mg/L*	Number of Retained Pairs	S_O, in mg/L	Bias, in mg/L	Bias, %	Statistically Significant
6	0.048	0.0488	0.0038	6	0.0034	0.001	1.7	no
6	0.128	0.1273	0.0015			–0.001	–0.5	no
10	0.80	0.815	0.038	10	0.029	0.015	1.9	no
10	1.28	1.310	0.068			0.030	2.3	no
11	3.20	3.242	0.071	10	0.031	0.042	1.3	no
10	4.80	4.829	0.100			0.029	0.6	no
10	6.08	6.157	0.093	10	0.067	0.077	1.3	yes
10	7.20	7.222	0.119			0.022	0.3	no

prepared in freshly boiled Type II water that was cooled and maintained with a helium purge. This material was sealed in ampoules under a nitrogen purge and sent to the participants. The participants were instructed to dilute 1 mL of the ampoule solution to 100 mL in water as specified under 8.2 of this test method.

15.6 Original 4000 mg/L formaldehyde ampoules of the same lot number as that used for the sample concentrates were sent for making the calibration standards for each of the participating laboratories.

15.7 One of the participating laboratories also did the analysis using the butanol extraction. The results are presented in Table X1.1 of the Appendix.

15.8 Several laboratories performed the titration in 8.6.1, independent of the collaborative study. The statistical results are given in Appendix X1. One of the laboratories also did a titration on the collaborative study calibration standard. The result is in Appendix X1.2.

15.9 Before this test method is applied to the analysis of samples, analysts shall establish their own precision and bias data.

16. Quality Assurance (QA)/Quality Control (QC)

16.1 Until such time as QA/QC procedures are established, it is recommended that the users refer to Practice D 4210 and Guide D 3856 as guides for establishing their own QA/QC.

16.2 A duplicate and known standard shall be run each day that a sample is analyzed. The duplicate and standard shall meet satisfactory limits as established by the control chart before an analysis is considered satisfactory.

16.3 A blank and spike shall be run each day that a sample is analyzed. The spike shall be in accordance with that outlined in Guide D 3856. The blank shall be low enough that it shall not unduly influence the data.

16.4 One standard should be run with every ten samples, or with each batch, whichever results in the greater frequency. The results shall meet satisfactory limits as established by 15.7 before the data for that batch or set of ten are acceptable.

16.5 Other formal QA/QC procedures will be incorporated at such time as they have been accepted officially by ASTM.

17. Keywords

17.1 formaldehyde

APPENDIX

(Nonmandatory Information)

X1. LABORATORY RESULTS

X1.1 An approximately 1100-mg/L formaldehyde solution was sent out to several laboratories to demonstrate the ability of the procedure in 8.6.1. The results are:

Laboratory results, mg/L:	1144
	1100
	1114
	1169
	1120
	1130
Mean:	1130
Standard Deviation:	24
RSD:	2.2%

X1.2 The results from a butanol extraction on the collaborative study samples from one of the participating laboratories is presented in Table X1.1. Most of the points are within one standard deviation of the mean for data reported under Table 1 of this test method. The result at 6.08 mg/L is an outlier to the data and also does not match with the aqueous determination.

TABLE X1.1 Formaldehyde With Butanol Extraction

Expected Amount in mg/L	Measured Amount in mg/L
0.80	0.80
1.28	1.29
3.20	3.19
4.80	4.93
6.08	6.57
7.20	7.27

X1.3 One of the laboratories performed a titration on the calibration standard sent out with the collaborative testing study. The titration was performed on a 1+9 dilution of standard into water. The mean result of three titrations was 400.7 mg/L with a RSD = 1.42 %. The manufacturer sold the

standard as 4000 ± 40 mg/L formaldehyde.