



Designation: **D3694 – 96 (Reapproved 2011) D3694 – 96 (Reapproved 2017)**

Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents¹

This standard is issued under the fixed designation D3694; 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 These practices cover the various means of (1) preparing sample containers used for collection of waters to be analyzed for organic constituents and (2) preservation of such samples from the time of sample collection until the time of analysis.

1.2 The sample preservation practice is dependent upon the specific analysis to be conducted. See Section 9 for preservation practices listed with the corresponding applicable general and specific constituent test method. The preservation method for waterborne oils is given in Practice D3325. Use of the information given herein will make it possible to choose the minimum number of sample preservation practices necessary to ensure the integrity of a sample designated for multiple analysis. For further considerations of sample preservation, see the *Manual on Water*.²

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 6.7, 6.24, and 8.1.3.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards*:³

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D1252 Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water

D1783 Test Methods for Phenolic Compounds in Water

D2036 Test Methods for Cyanides in Water

D2330 Test Method for Methylene Blue Active Substances (Withdrawn 2011)⁴

D2579 Test Method for Total Organic Carbon in Water (Withdrawn 2002)⁴

D2580 Test Method for Phenols in Water by Gas-Liquid Chromatography

D2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography

D3113 Test Methods for Sodium Salts of EDTA in Water (Withdrawn 2005)⁴

D3325 Practice for Preservation of Waterborne Oil Samples

D3371 Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography (Withdrawn 2002)⁴

D3534 Test Method for Polychlorinated Biphenyls (PCBs) in Water (Withdrawn 2003)⁴

D3590 Test Methods for Total Kjeldahl Nitrogen in Water

D3695 Test Method for Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

¹ These practices are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibilities of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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² *Manual on Water*. ASTM STP 442, ASTM, 1969. *Manual on Water*, ASTM STP 442, ASTM International, 1969.

³ 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 The last approved version of this historical standard is referenced on www.astm.org.

- D3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling
- D3921 Test Method For Oil and Grease and Petroleum Hydrocarbons in Water (Withdrawn 2013)⁴
- D3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water
- D4129 Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection
- D4165 Test Method for Cyanogen Chloride in Water
- D4193 Test Method for Thiocyanate in Water
- D4281 Test Method for Oil and Grease (Fluorocarbon Extractable Substances) by Gravimetric Determination (Withdrawn 2012)⁴
- D4282 Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion
- D4374 Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate (Withdrawn 2012)⁴
- D4515 Practice for Estimation of Holding Time for Water Samples Containing Organic Constituents (Withdrawn 2006)⁴
- D4657 Test Method for Polynuclear Aromatic Hydrocarbons in Water (Withdrawn 2005)⁴
- D4744 Test Method for Organic Halides in Water by Carbon Adsorption Microcoulometric Detection (Withdrawn 2002)⁴
- D4763 Practice for Identification of Chemicals in Water by Fluorescence Spectroscopy
- D4779 Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection (Withdrawn 2002)⁴
- D4839 Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection
- D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
- D4983 Test Method for Cyclohexylamine, Morpholine, and Diethylaminoethanol in Water and Condensed Steam by Direct Aqueous Injection Gas Chromatography (Withdrawn 2002)⁴
- D5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography
- D5176 Test Method for Total Chemically Bound Nitrogen in Water by Pyrolysis and Chemiluminescence Detection
- D5315 Test Method for Determination of N-Methyl-Carbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post-Column Derivatization
- D5316 Test Method for 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography
- D5317 Test Method for Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector
- D5412 Test Method for Quantification of Complex Polycyclic Aromatic Hydrocarbon Mixtures or Petroleum Oils in Water
- D5475 Test Method for Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector (Withdrawn 2011)⁴
- D5790 Test Method for Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry
- D5812 Test Method for Determination of Organochlorine Pesticides in Water by Capillary Column Gas Chromatography (Withdrawn 2011)⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology [D1129](#).

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4. Significance and Use

4.1 There are four basic steps necessary to obtain meaningful analytical data: preparation of the sample container, sampling, sample preservation, and analysis. In fact these four basic steps comprise the analytical method and for this reason no step should be overlooked. Although the significance of preservation is dependent upon the time between sampling and the analysis, unless the analysis is accomplished within 2 h after sampling, preservation is preferred and usually required.

5. Apparatus

5.1 *Forced Draft Oven*, capable of operating at 275 to 325°C.

5.2 *Sample Bottle*, borosilicate or flint glass.

NOTE 1—High density polyethylene (HDPE) bottles and caps have been demonstrated to be of sufficient quality to be compatible for all tests except pesticides, herbicides, polychlorinated biphenyls, and volatile organics. However, this bottle cannot be recycled.

5.3 *Sample Bottle Cap*, TFE-fluorocarbon or aluminum foil-lined.

NOTE 2—Even these liners have some disadvantages. TFE is known to collect some organic constituents, for example, PCBs. Aluminum foil will react

with samples that are strongly acid or alkaline. Clean TFE liners as described in 7.1. Replace aluminum foil with new foil after each use.

5.4 *Sample Vial*, glass.

5.5 *Septa*, PTFE-faced with screw cap lid and matching aluminum foil disks.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in 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.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification **D1193**, Type II and demonstrated to be free of specific interference for the test being performed.

6.3 *Acetic Acid Buffer Solution* (pH 4)—Dissolve 6.0 g of sodium acetate in 75 mL of water. Add 30 mL of glacial acetic acid, with stirring.

6.4 *Acetone*.

6.5 *Acid Buffer Solution* (pH 3.75)—Dissolve 125 g of potassium chloride and 70 g of sodium acetate trihydrate in 500 mL of water. Add 300 mL of glacial acetic acid and dilute to 1 L.

6.6 *Ascorbic Acid*.

6.7 *Chromic Acid Cleaning Solution*—To a 2-L beaker, add 35 mL of saturated sodium dichromate solution followed by 1 L of sulfuric acid (sp gr 1.84) with stirring. (**Warning**—Use rubber gloves, safety goggles, and protective clothing when preparing and handling this corrosive cleaning agent that is a powerful oxidant. Store the reagent in a glass bottle with a glass stopper.)

6.8 *Detergent*, formulated for cleaning laboratory glassware.

6.9 *Hydrochloric Acid*—Concentrated HCl (sp gr 1.19).

6.10 *Hydrochloric Acid* (1 + 2)—To 200 mL of water, carefully add 100 mL of hydrochloric acid (see 6.9). Store in a glass-stoppered reagent bottle.

6.11 *Ice*, crushed wet.

6.12 *Lead Acetate Test Paper*.

6.13 *Lead Acetate Solution*—Dissolve 50 g of lead acetate in water and dilute to 1 L.

6.14 *Lead Carbonate*, powdered.

6.15 *Lime, Hydrated*, powdered.

6.16 *Mercuric Chloride*.

6.17 *Monochloroacetic Acid Buffer* (pH 3)—Prepare by mixing 156 mL of chloroacetic acid solution (236.2 g/L) and 100 mL of potassium acetate solution (245.4 g/L).

6.18 *Nitric Acid*—Concentrated HNO₃ (sp gr 1.42).

6.19 *Phosphate Buffer*—Dissolve 138 g of sodium dihydrogen phosphate in water and dilute to 1 L. Refrigerate this solution.

6.20 *Phosphate Solution*—Dissolve 33.8 g of potassium dihydrogen phosphate in 250 mL of water.

6.21 *Phosphoric Acid*—Concentrated H₃PO₄ (sp gr 1.83).

6.22 *Phosphoric Acid Solution* (1 + 1)—Dilute 1 vol of phosphoric acid (sp gr 1.83).

6.23 *pH Paper*, narrow range for pH < 2, pH > 12, and pH 5 to 7.

6.24 *Potassium Iodide—Starch Test Paper*.

6.25 *Sodium Bisulfate*.

6.26 *Sodium Bisulfite Solution*—Dissolve 2 g of sodium bisulfite in 1 L of water and adjust to pH 2 by the slow addition of H₂SO₄ (1 + 1). (**Warning**—Prepare and use this reagent in a well ventilated hood to avoid exposure to SO₂ fumes.)

6.27 *Sodium Sulfite Solution* (0.1 M)—Transfer approximately 10.3 g of sodium sulfite to a 1-L volumetric flask. Dilute to volume with water.

⁵ *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.

6.28 *Sodium Thiosulfate*.

6.29 *Sodium Hydroxide Pellets*.

6.30 *Mercuric Chloride* (10 mg/mL)—Dissolve 100 mg of HgCl_2 in reagent water and dilute to 10 mL.

6.31 *Sulfuric Acid* (1 + 1)—Slowly and carefully add 1 vol of sulfuric acid (see 6.27) to 1 vol of water, stirring and cooling the solution during addition.

7. Preparation of HDPE Sample Bottles

7.1 Wash the bottles with two 100-mL portions of HCl (1 + 2) and rinse with three 100-mL portions of water. These volumes of wash and rinse portions are recommended for 1-L sample bottles; therefore, use proportionate volumes for washing and rinsing sample bottles of a different volume.

8. Preparation of Glass Sample Bottles and Vials

8.1 *Solvent-Detergent/Chromic Acid Preparation of Glass Sample Bottles:*

8.1.1 Rinse the container with 100 mL of dilute detergent or acetone. For some residues, a few alternative detergent and acetone rinses may be more satisfactory. Then rinse at least three times with tap water followed by a reagent water rinse to remove the residual detergent or acetone, or both.

8.1.2 Rinse the container with 100 mL of chromic acid solution, returning the chromic acid to its original container after use. Then rinse with at least three 100-mL portions of tap water followed by a reagent water rinse.

8.1.3 Rinse the container with 100 mL of NaHSO_3 solution to remove residual hexavalent chromium. (**Warning**—Carry out this step in a hood to prevent exposure to SO_2 fumes.)

8.1.4 Rinse the container with water until sulfurous acid and its vapors have been removed. Test rinsings for acid with a pH meter or an appropriate narrow range pH paper. Rinsings should have a pH approximately the same as the water used for rinsing.

8.1.5 When the last trace of NaHSO_3 has been removed, wash with three additional 100-mL portions of water. Allow to drain. This procedure is for 1-L sample containers, therefore, use proportionate volumes for washing and rinsing sample containers of a different volume.

8.1.6 Heat for a minimum of 4 h (mouth up) in a forced draft oven at 275 to 325°C. Upon cooling, fit the bottles with caps and the vials with septa.

NOTE 3—For some tests, heating may not be required. Refer to the individual method to determine the necessity for this treatment.

8.2 *Machine Washing Glass Sample Bottles and Vials:*

NOTE 4—Machine washing of narrow mouth sample bottles may not yield acceptable results.

8.2.1 Rinse the container with 100 mL of chromic acid solution, returning the chromic acid to its original container after use. Then rinse with at least three 100-mL portions of tap water.

8.2.2 Machine wash in accordance with the machine manufacturer's instructions using a detergent and 90°C water.

8.2.3 Remove the bottles from the machine and rinse them with two 100-mL portions of HCl (1 + 2), followed with three 100-mL portions of water.

8.2.4 Heat for a minimum of 4 h (mouth up) in a forced draft oven at 275 to 325°C. Upon cooling, fit the bottles with caps and the vials with septa (see Note 3).

9. Sample Preservation

9.1 Depending upon the type of analysis required, use any one or a combination of the following methods of sample preservation (see Tables 1-3, Annex A1, and Annex A2).

9.1.1 Adjust the pH. An adjustment to neutral pH is usually prescribed when chemical reactions, such as hydrolysis, are to be avoided. Adjustment to an extreme pH, for example, <2, is usually prescribed to inhibit biological activity for biodegradable organic chemicals.

NOTE 5—To confirm the adjustment of the pH of samples to the proper value, place a drop of sample on an appropriate pH test paper or measure with a pH meter.

9.1.1.1 *Sulfuric Acid*—To the sample bottle partially filled with sample, slowly add 2 mL of H_2SO_4 (sp gr 1.84) and mix thoroughly. Confirm that the pH is less than 2. If the pH is greater than 2, add additional acid until the pH is less than 2. This procedure is based on a 1-L sample bottle; therefore, use proportionate volumes for sample bottles with a different volume.

9.1.1.2 *Hydrochloric Acid*—To a sample bottle partially filled with sample, add 6 mL of HCl (sp gr 1.19) while swirling the bottle. After the acid addition, confirm that the pH is less than 2. If the pH is greater than 2, add additional acid to lower the pH to less than 2. This procedure is for a 1-L sample bottle; therefore, use proportionate volumes for sample bottles with a different volume.

9.1.1.3 *Sodium Bisulfate*—To a sample bottle partially filled with sample, add approximately 9 g of NaHSO_4 . Mix to dissolve and confirm that the pH is less than 2. If the pH is greater than 2, add additional NaHSO_4 until the pH is less than 2. This procedure is based on a 1-L sample bottle, therefore, use proportionate amounts for sample bottles with a different volume.