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An American National Standard

Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[1]

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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 D 3325. 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 *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.* For specific hazard statements, see 6.7, 6.24, and 8.1.3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 1252 Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water[4]
D 1783 Test Methods for Phenolic Compounds in Water[4]
D 2036 Test Methods for Cyanides in Water[4]
D 2330 Test Method for Methylene Blue Active Substances[4]
D 2579 Test Methods for Total and Organic Carbon in Water[4]
D 2580 Test Method for Phenols in Water by Gas-Liquid Chromatography[4]
D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[4]
D 3113 Test Methods for Sodium Salts of EDTA in Water[4]
D 3325 Practice for Preservation of Waterborne Oil Samples[4]
D 3371 Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography[4]
D 3534 Test Method for Polychlorinated Biphenyls (PCBs) in Water[4]
D 3590 Test Methods for Total Kjeldahl Nitrogen in Water[4]
D 3695 Test Method for Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography[4]
D 3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling[4]
D 3921 Test Method for Oil and Grease and Petroleum Hydrocarbons in Water[4]
D 3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water[4]
D 4129 Test Method for Total and Organic Carbon in Water by High-Temperature Oxidation and Coulometric Detection[4]
D 4165 Test Method for Cyanogen Chloride in Water[4]
D 4193 Test Method for Thiocyanate in Water[4]
D 4281 Test Method for Oil and Grease (Fluorocarbon Extractable Substances) by Gravimetric Determination[4]
D 4282 Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion[4]
D 4374 Test Methods for Cyanide in Water—Automated Methods for Total Cyanide, Dissociable Cyanide, and Thiocyanate[4]
D 4515 Practice for Estimation of Holding Time for Water Samples Containing Organic Constituents[4]
D 4657 Test Method for Polynuclear Aromatic Hydrocarbons in Water[4]
D 4744 Test Method for Organic Halides in Water by Carbon Adsorption Microcoulometric Detection[4]
D 4763 Practice for Identification of Chemicals in Water by Fluorescence Spectroscopy[4]

[1] These practices are under the jurisdiction of ASTM Committee D-19 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.

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

[4] *Annual Book of ASTM Standards*, Vol 11.02.

D 4779 Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection[4]
D 4839 Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection[4]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]
D 4983 Test Method for Cyclohexylamine, Morpholine, and Diethylaminoethanol in Water and Condensed Steam by Direct Aqueous Injection Gas Chromatography[4]
D 5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography[4]
D 5176 Test Method for Total Chemically Bound Nitrogen in Water by Pyrolysis and Chemiluminescence Detection[4]
D 5315 Test Method for *N*-Methyl-Carbamoyloximes and *N*-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post-Column Derivation[4]
D 5316 Test Method for 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography[4]
D 5317 Test Method for the Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector[4]
D 5412 Test Method for Quantification of Complex Polycyclic Aromatic Hydrocarbon Mixtures or Petroleum Oils in Water[4]
D 5475 Test Method for Nitrogen and Phosphorus Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector[4]
D 5790 Test Method for Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry[4]
D 5812 Test Method for Determination of Organochlorine Pesticides in Water by Capillary Column Gas Chromatography[4]

3. Terminology

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

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 D 1193, 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.

[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.

6.15 *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 HNO_3(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 H_3PO_4(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 H_2SO_4(1 + 1). **Warning**—Prepare and use this reagent in a well ventilated hood to avoid exposure to SO_2 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.

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.

TABLE 1 Recommended Preservation Practice for General Organic Constituent Test Methods

NOTE 1—The container preparation procedures described in Sections 7 and 8 should yield bottles of sufficient quality to be compatible with the test methods listed in this table. However, a sample bottle blank should be obtained to establish the fact.

Test Method(s)	Recommended Practice
D 1252, Oxygen demand, chemical	9.1.1.1 sulfuric acid or 9.1.1.3 sodium bisulfate or 9.1.3 refrigeration
D 2579, Organic carbon, total, by combustion-infrared or reduction-FID	9.1.3 refrigeration
D 3921, Oil and grease, petroleum hydrocarbons	9.1.1.1 sulfuric acid (1 + 1) or 9.1.1.3 sodium bisulfate
D 4129, Total and organic carbon, oxidation coulometric	9.1.3 refrigeration and 9.1.4 hermetically sealing, zero headspace
D 4281, Oil and grease, gravimetric	9.1.1.1 sulfuric acid or 9.1.1.2 hydrochloric acid
D 4744, Organic halides, by carbon absorption-microcoulometry	9.1.1.8 nitric acid and 9.1.2 sodium sulfite and 9.1.3 refrigeration
D 4763, Identification by fluorescence	9.1.3 refrigeration
D 4779, Carbon, total, organic and inorganic in high-purity water	9.1.1.8 nitric acid and 9.1.3 refrigeration
D 4839, Carbon, total and organic in water	9.1.3 refrigeration and either 9.1.1.1 [A] sulfuric acid or 9.1.1.5 phosphoric acid or 9.1.1.8 nitric acid
D 5176 Nitrogen, total chemically-bound, pyrolysis-chemiluminescence	9.1.1.1 sulfuric acid or 9.1.1.2 hydrochloric acid, and 9.1.3 refrigeration
PS 48, Oil and grease (solvent extractable substances) by gravimetric determination	9.1.1.1 sulfuric acid (1 + 1) or 9.1.1.2 hydrochloric acid (1 + 1)

[A] Acidification can be used only when organic carbon alone is being determined. If total carbon is of interest, the sample must not be acidified; refrigeration is the only appropriate preservation technique.

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.

9.1.1.4 *Sodium Hydroxide*—Adjust the sample pH to above 12 using NaOH (pellets). Store the sample away from light.

9.1.1.5 *Phosphoric Acid*—To a sample bottle partially filled with sample, slowly add 2 mL of phosphoric acid (sp gr 1.83) 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.

9.1.1.6 *Phosphate Buffer*—Reduce pH to 8.0 to 8.5 range with careful additions of phosphate buffer.

9.1.1.7 *Acid Buffer*—Add 4 mL per 100 mL of sample.

9.1.1.8 *Nitric Acid*—To a sample bottle partially filled with sample, slowly add 2 mL of nitric acid (sp gr 1.42) 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.

9.1.1.9 *Phosphate/Phosphoric Acid*—Add approximately 1 mL phosphate solution followed by a few drops of 1 + 1 phosphoric acid solution to 115 mL of water sample to bring the pH to approximately 3.

TABLE 2 Recommended Preservation Practice for Specific Organic Constituent Test Methods

Test Method(s)	Recommended Practice
D 1783 Phenolic compounds by 4-AAP	9.1.3 refrigeration and 9.1.1.1 sulfuric acid or 9.1.1.3 sodium bisulfate or 9.1.1.2 hydrochloric acid or 9.1.1.5 phosphoric acid
D 2036 [A] Cyanide	9.1.1.4 sodium hydroxide and in presence of chlorine 9.1.2 chlorine removal
D 2330 Alkyl benzene sulfonate	9.1.1.1 sulfuric acid or 9.1.1.3 sodium bisulfate
D 2580 Phenols by gas liquid chromatography	9.1.3 refrigeration
D 2908 Volatile organic matter in water by aqueous injection gas chromatography (DAIGC)	9.1.3 refrigeration and 9.1.1.1 sulfuric acid or 9.1.1.3 sodium bisulfate
D 3086 Pesticides, organochlorine	9.1.3 refrigeration
D 3113 Ethylenediaminetetraacetate	9.1.3 refrigeration
D 3371 Nitriles by DAIGC	9.1.3 refrigeration and 9.1.1.1 sulfuric acid or 9.1.1.3 sodium bisulfate
D 3534 Polychlorinated biphenyls	9.1.3 refrigeration
D 3590 Total nitrogen, Kjeldahl	9.1.3 refrigeration and 9.1.1.1 sulfuric acid
D 3695 Volatile alcohols by DAIGC	9.1.3 refrigeration and 9.1.1.1 sulfuric acid or 9.1.1.3 sodium bisulfate
D 3871 Purgeable organic compounds	9.1.2 chlorine removal, 9.1.3 refrigeration, 9.1.4 hermetically sealing
D 3973 Low molecular weight hydrocarbons	9.1.3 refrigeration, and in presence of chlorine 9.1.2 chlorine removal and 9.1.4 hermetically sealing, zero headspace
D 4165 Cyanogen chloride	9.1.1.6 phosphate buffer to ph 8.0 to 8.5
D 4193 Thiocyanate	9.1.1.2 acid or 9.1.1.4 base
D 4282 Free cyanide	9.1.3 refrigeration, 9.1.1.4 sodium hydroxide, and 9.1.5 in dark
D 4374 Total dissociable cyanide, automated	9.1.3 refrigeration and 9.1.1.4 sodium hydroxide, in dark
D 4657 Polynuclear aromatic hydrocarbons	9.1.3 refrigeration, 9.1.1.2 acid, or 9.1.1.4 sodium hydroxide (to pH 6.0 to 8.0), 9.1.2 chlorine removal
D 4983 Cyclohexamine, morpholine, diethanolamine by DAI	9.1.1.9 phosphate/phosphoric acid and 9.1.3 refrigeration.
D 5175 Organohalide pesticides and PCBs	9.1.2 chlorine removal and 9.1.3 refrigeration
D 5315 Carbamate pesticides	9.1.2 chlorine removal, 9.1.3 refrigeration
D 5316 EDB and DBCP	9.1.1.2 chlorine removal, 9.1.2 chlorine removal, 9.1.3 refrigeration, hermetic seal
D 5317 Chlorinated Acids	9.1.2 chlorine removal, 9.1.3 refrigeration, 9.1.6 mercuric chloride
D 5412 PAH mixtures	9.1.3 refrigeration (5C)
D 5475 Nitrogen/phosphorus pesticides	9.1.2 chlorine removal, 9.1.3 refrigeration, 9.1.6 mercuric chloride
D 5790 Purgeable organic compounds by GC/MS	9.1.1.2 hydrochloric acid, 9.1.2 chlorine removal, 9.1.3 refrigeration, 9.1.4 hermetic seal
D 5812 Organochlorine pesticides by GC	9.1.2 chlorine removal, 9.1.3 refrigeration, 9.1.6 mercuric chloride

[A] See Annex A1 for alternative treatment if the sample is suspected to contain sulfide or a high concentration of carbonate.

9.1.1.10 *Monochloroacetic Acid Buffer*—Add 1.8 mL of monochloroacetic acid buffer solution (pH 3) to a 60-mL sample bottle prior to filling.

9.1.1.11 *Biocide*—Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L.

9.1.2 *Chlorine Removal*—Chlorine is added to water supplies and discharges as a disinfectant and oxidant for organic compounds. If the chlorine is not eliminated at the time of sampling, chlorination of organics present in the sample may occur; that is, trihalomethanes and chlorophenols will form, causing a positive interference for these analytes. Test a drop of

TABLE 3 Maximum Holding Times Allowed by ASTM Test Methods and EPA Regulations

Test Method(s)	Holding Times	
	In Standard	In 40 CFR 136 [A]
D 1252 Oxygen demand, chemical	24 h if not acidified	28 days
D 1783 Phenolic compounds by 4-AAP	28 days	28 days
D 2036 Cyanide	None stated	NA
D 2330 Alkyl benzene sulfonate	7 days	NA [B]
D 2579 Organic carbon, total by combustion-infrared or reduction-FID	None stated	28 days
D 2580 Phenols by gas liquid chromatography	Keep to minimum	28 days
D 2908 Volatile organic matter in water by aqueous injection gas chromatography (DAIGC)	Keep to minimum	NA
D 3113 Ethylenediaminetetracetate	15 min recommended	NA
D 3371 Nitriles by gas liquid chromatography by DAIGC	Keep to minimum	NA
D 3534 Polychlorinated biphenyls	None stated	7 days for extraction, 40 days after extraction
D 3590 Total nitrogen, Kjeldahl	28 days	28 days
D 3695 Volatile alcohols by DAIGC	None stated	NA
D 3871 Purgeable organic compounds	None stated	14 days
D 3921 Oil and grease, petroleum hydrocarbons	None stated	28 days
D 3973 Low molecular weight hydrocarbons	15 days	14 days
D 4129 Total and organic carbon, oxidation coulometry	None stated	28 days
D 4165 Cyanogen chloride	Immediate analysis recommended	NA
D 4193 Thiocyanate	None stated	NA
D 4281 Oil and grease, gravimetric	Up to 2 months	28 days
D 4282 Free cyanide	Immediate analysis recommended	14 days
D 4374 Total dissociable cyanide, automated	Immediate analysis recommended	14 days
D 4657 Polynuclear aromatic hydrocarbons	7 days for extraction, 30 days for analysis	7 days for extraction, 40 days after extraction
D 4744 Organic halides, by carbon absorption-microcoulometry	7 days	NA
D 4763 Identification by fluorescence	None stated	NA
D 4779 Carbon, total, organic and inorganic, in high purity water	None stated	28 days
D 4839 Carbon, total and organic, in water	None stated	28 days
D 4983 Cyclohexamine, morpholine diethanolamine by DAI	None stated	NA
D 5175 Organohalide pesticides and PCBs	7 days	7 days
D 5176 Nitrogen chemically bound	None stated	NA
D 5315 N-methyl-carbamoyloximes and N-methylcarbamates by HPLC	28 days	NA
D 5316 1,2-dibromoethane and 1,2-dibromo-3-chloropropane by GC	28 days	NA
D 5317 Chlorinated organic acid compounds by GC	14 days for extraction, 28 days for analysis	7 days for extraction, 40 days after extraction
D 5475 Nitrogen and phosphorous containing pesticides by GC	14 days for extraction, 14 days for analysis	NA
D 5790 Purgeable organic compounds by GC/MS	14 days	14 days (refer to Part 136, Table II for exceptions)
D 5812 Organochlorine pesticides by GC	7 days for extraction, 14 days for analysis	7 days for extraction, 40 days after extraction

[A] Title 40, Code of Federal Regulations, Part 136 (40 CFR 136), by the U.S. Environmental Protection Agency.
[B] NA = Not applicable.

the sample with potassium iodide-starch paper; a blue color indicates the need for the following treatment: add ascorbic acid, dissolving a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.05 g of ascorbic acid[6] per litre of sample. Alternatively, sodium sulfite solution (0.1 *M*) is used; typically, 0.2 mL/100 mL of sample is sufficient. Sodium thiosulfate (3 mg/40 mL) is used to remove chlorine from pesticide/PCB samples. Sodium thiosulfate (3 mg/40 mL) is used to remove chlorine from pesticide/PCB samples.

9.1.3 *Refrigeration at 4°C*— Samples are cooled to reduce biological activity on the organic chemicals. Cool the sample to 4°C immediately after sampling using a wet ice water bath. During storage or shipment, or both, maintain the sample at 4°C. Prior to the analysis, raise the sample temperature to room temperature using a water bath with a temperature no more than 5°C above room temperature. If the sample temperature is not adjusted, then an appropriate temperature-volume correction must be made.

9.1.4 *Hermetically Sealing (Purgeable Organics)*—Add required preservatives to a sample vial. Fill the vial to overflowing so that a convex meniscus forms at the top. Place a septum, PTFE side down, carefully on the opening of the vial, displacing the excess water. Seal the vial with the screw cap and invert to verify the seal by demonstrating the absence of air bubbles (zero headspace).

9.1.5 *Minimize Photodecomposition*—Collect samples in dark bottles and store in the dark.

9.1.6 *Mercuric Chloride*—Mercuric chloride (1 mL of a 10 mg/mL mercuric chloride solution) should be added to a 1-L sample bottle prior to sample collection if biological degradation of the target analytes may occur. Mercuric chloride is a highly toxic chemical and must be handled with caution. Samples containing mercuric chloride must be disposed of properly.

10. Sample Holding Times

10.1 Table 3 lists maximum holding times prescribed in ASTM standards for measuring organic compounds in water. The applicable holding times cited in the U.S. EPA "Guidelines

[6] Do not use ascorbic acid when organic carbon is to be determined.

Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act"[7] are also included in Table 3.

10.2 Samples that exceed holding times should be discarded rather than analyzed.

10.3 Holding times for organic constituents are highly dependent upon the chemical and biological composition of the sample. Sample holding times for a specific matrix may be determined by using the procedure described in Practice D 4515 or D 4841. These practices are particularly useful when sampling, transporting, or scheduling complications make it desirable to have holding times beyond those prescribed in the test method.

[7] "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act," Title 40, Code of Federal Regulations, Part 136.3(e), written by the U.S. Environmental Protection Agency, available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20401.

11. Keywords

11.1 organic constituents; sample containers; sample preservation

ANNEXES

(Mandatory Information)

A1. ALTERNATIVE TREATMENT STEPS

A1.1 Table A1.1 gives a list of additional or alternative treatment steps that are required in the presence of specific interfering constituents:

TABLE A1.1 Alternate Treatment Steps

Test Method(s)	Interfering Constituent	Recommended Treatment for Preservation
D2036 Cyanide	sulfide	Sulfide in the sample can convert CN^- to SCN^-, especially at high pH. Before stabilizing the sample by raising the pH for the preservation of the cyanide content, test for sulfide by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution (pH 4). Darkening of the paper indicates the presence of sulfide. (The simultaneous presence of both sulfide and oxidizing agents is not anticipated. Oxidizing agents should be also removed before sample preservation.) Sulfide is removed by adding lead acetate solution (50 g/L) a drop at a time; retest on the test paper and continue until a negative paper test has been read, add 1 drop in excess and immediately filter out the black lead sulfide precipitate. If sulfide content is high, add instead powdered lead carbonate to avoid significant reduction of the pH. After sulfide removal, continue with 9.1.1.5.
	high carbonate content	When sampling effluents such as coal gasification wastes, atmospheric emission scrub waters, and other high carbonate content wastes, use hydrated lime in the powder form to stabilize the sample instead of NaOH. Add slowly with stirring to raise the pH to 12 to 12.5. Decant the sample into the sample bottle after the precipitate has been settled. High carbonate content affects the distillation procedure by causing excessive gasing when the acid is added. The CO_2 released also may significantly reduce the NaOH content in the adsorbent.)

A2. PRESERVATION OF COMPOSITE SAMPLES

A2.1 When composite samples are collected, the appropriate preservation reagents must be added to the compositing vessel prior to collection. If the preservation requirements call for refrigeration, the sample must be refrigerated during collection. The collection time for a single composite sample shall not exceed 24 h. If longer sampling periods are necessary, a series of composite samples shall be collected.