



Designation: D 7365 – 07

Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide¹

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1. Scope

1.1 This practice is applicable for the collection and preservation of water samples for the analysis of cyanide. This practice also addresses the mitigation of known interferences prior to the analysis of cyanide.

1.2 The sampling, preservation and mitigation of interference procedures described in this practice are recommended for the analysis of total cyanide, available cyanide, weak acid dissociable cyanide, and free cyanide by Test Methods **D 2036**, **D 4282**, **D 4374**, **D 6888**, **D 6994**, and **D 7237**. This practice can also be applied to other cyanide methods, for example, US EPA Method 335.4 and Standard Methods 4500-CN⁻ C.

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 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 1193** Specification for Reagent Water
 - D 1293** Test Methods for pH of Water
 - D 2036** Test Methods for Cyanides in Water
 - D 3370** Practices for Sampling Water from Closed Conduits
 - D 3694** Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
 - D 3856** Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water

- D 4282** Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion
 - D 4374** Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate
 - D 4411** Guide for Sampling Fluvial Sediment in Motion
 - D 4840** Guide for Sample Chain-of-Custody Procedures
 - D 4841** Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
 - D 6888** Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
 - D 6994** Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection
 - D 6696** Guide for Understanding Cyanide Species
 - D 7237** Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
- 2.2 *U.S. EPA Methods:*³
- EPA OIA-1677
 - EPA Method 335.2
 - EPA Method 335.4
- 2.3 *APHA Standard:*⁴
- Standard Methods 4500-CN Methods C, D, E, F, G, and I
- 2.4 *USGS Methods:*⁵
- USGS I-3300-85
 - USGS I-4302-85

3. Terminology

3.1 Definitions:

¹ This practice is under the jurisdiction of ASTM Committee D19 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.

³ Available from United States Environmental Protection Association (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, www.epa.gov.

⁴ Standard Methods for the Examination of Water and Wastewater, 21st edition (2005), American Public Health Association (APHA), 800 I Street, NW Washington, DC 20001, www.apha.org.

⁵ Available from United States Geological Survey, 12201 Sunrise Valley Drive, Reston, VA, 20192, www.usgs.gov.

For definitions of terms used in this practice, refer to Terminology **D 1129** and Guide **D 6696**.

3.2 In this practice, refrigeration shall designate storing the sample between its freezing point and 6°C.

4. Summary of Practice

4.1 Samples are collected in appropriate containers, mitigated for known interferences, and stabilized with sodium hydroxide prior to analysis.

5. Significance and Use

5.1 Cyanide is routinely analyzed in water samples, often to demonstrate regulatory compliance; however, improper sample collection or pretreatment can result in significant positive or negative bias potentially resulting in unnecessary permit violations or undetected cyanide releases into the environment.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this practice. 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.⁶ 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, references to water shall be understood to mean reagent water that meets the purity specifications of Type I or Type II water, presented in **D 1193**.

6.3 *Acetate Buffer*—Dissolve 410 g of sodium acetate trihydrate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) in 500 mL of water. Add glacial acetic acid to yield a solution pH of 4.5, approximately 500 mL.

6.4 *Lead Acetate Test Strips*—Turns black in presence of sulfides. Moisten the paper with acetate buffer prior to use. Lead acetate test strips have been shown to be sensitive to about 50 mg/L S^{2-} .

6.5 *Potassium Iodide (KI) Starch Test Paper*—Turns blue in presence of free chlorine. Commercial alternative test strips may be used if they are shown to be at least as sensitive as the KI starch test strips.

6.6 *pH Indicator Test Strips*—pH indicator test strips capable of changing color at 0.5 pH units in the range of pH 10 to 14. More than one test strip may be necessary to cover this range.

6.7 *Sodium Hydroxide Solution (5 % wt/vol)*—In a 1 L volumetric flask, dissolve 50 g NaOH in reagent water and dilute to volume.

6.8 *Sodium Hydroxide Solution (50 % wt/vol)*—In a beaker, dissolve 50 g NaOH in reagent water not to exceed 100 mL total volume, then transfer to a 100-mL volumetric flask and

dilute to volume. **Warning**—This is an exothermic reaction and the solution will become very hot while being prepared. It is recommended to place the solution in a water bath to cool.

6.9 *Hydrated Lime*— $\text{Ca}(\text{OH})_2$ powder.

6.10 *Cadmium chloride*, CdCl_2 .

6.11 *Ethylenediamine (EDA)*

6.12 *Reducing Agents*—Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), ascorbic acid, sodium arsenite (NaAsO_2), or sodium borohydride (NaBH_4).

6.13 *Filter Paper or Syringe equipped with Leur-Lock Filters*—Unless specified, 0.45 μm pore size.

6.14 *Acidification Reagents*—Concentrated hydrochloric acid (HCl) or concentrated sulfuric acid (H_2SO_4).

6.15 *Sample Bottles*—See section 8.2 for further information about sample bottles.

7. Hazards

7.1 **Warning**—Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). Adequate ventilation is necessary when handling cyanide solutions and a fume hood should be utilized whenever possible.

7.2 **Warning**—Many of the reagents used in these test methods are highly toxic. These reagents and their solutions must be disposed of properly.

8. Procedure

8.1 Laboratory personnel and field samplers should follow the practices described in Guide **D 3856**. When sampling closed conduits such as process streams refer to Practice **D 3370**. When sampling fluvial sediment in motion or open channel flow refer to Guide **D 4411**. It is recommended to consult with the analytical laboratory prior to collecting samples to ensure the proper sample volume, containers, preservatives, etc., as these parameters may vary depending on the analytical methods used to measure the cyanide.

8.2 *Sample Containers:*

8.2.1 Sample containers shall be made of materials that will not contaminate the sample, cleaned thoroughly to remove all extraneous surface contamination prior to use. Chemically resistant glass containers are suitable as well as rigid or collapsible plastic containers made of polyethylene or polypropylene.

8.2.2 Virgin commercially cleaned containers certified to be free of contamination are recommended; otherwise, wash containers with soap or biodegradable detergent if required, then dry by draining. For further information on sample containers, see Practices **D 3694**.

8.2.3 Samples should be collected and stored in dark bottles to minimize exposure to ultraviolet radiation.

8.3 *Sample Collection, Preservation, and Mitigation of Interferences:*

8.3.1 Collect a sample volume that is sufficient to the analytical method into a sample bottle described above. If the required sample volume is not specified, usually 1L is sufficient for most analytical test methods, however, flow injection and automated methods usually consume considerably less sample volume than manual methods.

⁶ *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.

8.3.2 Certain sample matrices may require immediate analysis to avoid cyanide degradation due to interferences. While holding times are specified in this practice, it is recommended to estimate the actual holding time for each sample matrix as described in Practice [D 4841](#). A holding time study is required for any sample matrix showing evidence that the holding time is less than presented in this practice. Potential interferences and their corresponding analytical methods are shown in [Table 1](#). In the absence of interference, simple cyanides such as HCN, KCN, and NaCN are determined readily by each of the determinative steps, however, to determine “total” cyanide, metal cyanide bonds must be broken and cyanide separated to produce simple cyanide. In most total cyanide methods, this is accomplished by distillation from acid solution. Although distillation is assumed to eliminate or at least minimize most interferences, the high temperature and strong acid solutions can potentially introduce significant positive or negative bias. Interferences for total cyanide by distillation are listed in [Tables 2 and 3](#). Interferences are also dependent on the determinative step, which are shown in [Table 4](#).

8.3.3 There may be interferences that are not mitigated by this procedure. Any removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal technique not described in this practice or the analytical test method should be documented along with supporting data.

8.3.4 If the sample can be analyzed within 48 h and sulfide is not present, adjust the pH to 12–13 with sodium hydroxide (for example, 5 % NaOH or 50 % NaOH). For aquatic free cyanide by Test Method [D 7237](#), adjust to pH 11 as specified in the test method. Verify the pH of each sample with pH indicator test strips or by Test Methods [D 1293](#). Refrigerate the sample and analyze within 48 h.

8.3.5 Otherwise, to extend the holding time to 14 days and mitigate interferences, treat the sample immediately using any or all of the following techniques as necessary, followed by adjustment of the sample to pH 12–13 and refrigeration.

8.3.6 *Sulfide*—Test for the presence of sulfide by placing a drop of sample on a lead acetate test strip that has been previously moistened with acetate buffer. If the test strip turns black, sulfide is present (above 50 mg/L S^{2-}) and treatment is necessary as described in sections [8.3.6.1](#) or [8.3.6.2](#). If the test is negative and there are no further interferences suspected, adjust the pH to 12–13, refrigerate, and ship or transport to the laboratory.

8.3.6.1 If the sample contains sulfide as indicated with a lead acetate test strip or is known to contain sulfides that will interfere with the test method, dilute the sample with reagent water until the lead acetate test strip no longer indicates the presence of sulfide (<50 mg/L S^{2-}) or until the interference is no longer significant to the analytical test method. For example, add 200 mL of freshly collected sample into a bottle containing 800 mL of reagent water, then test for sulfide again as indicated in [8.3.6](#). If the test for sulfide is negative, adjust the pH to 12–13, refrigerate, and ship or transport to the laboratory. If the test for sulfide is still positive, further dilution is

required; however, be careful not to over dilute the sample as the detection limit will be elevated by this factor. In the aforementioned example, the dilution factor would be equal to 5 (total volume/sample volume). Clearly indicate the dilution volumes on the sample and chain-of-custody form so that the laboratory can mathematically correct the result.

8.3.6.2 Alternatively, sulfide can be removed by precipitation if free cyanide is the only form of cyanide to be measured (for example, Test Method [D 7237](#)). For removal of sulfide by precipitation, if the pH is less than pH 11, raise the pH to 11 with NaOH solution, and then add approximately 1 mg of powdered cadmium chloride for each mL of sample. Cap and shake the container to mix. Allow the precipitate to settle and test the sample with lead acetate paper for residual sulfide. If necessary, add more cadmium chloride but avoid adding excess. Finally, filter through a 0.45 μ m filter. Refrigerate, then transport or ship the filtrate to the laboratory.

NOTE 1—Some analytical methods prescribe the use of lead carbonate or lead acetate to precipitate sulfide; however, sulfide and cyanide can form thiocyanate in the presence of lead causing decreased cyanide recoveries; therefore, lead carbonate and lead acetate should be avoided. Methods that specify the addition of bismuth nitrate to treat sulfide during total cyanide distillations have been demonstrated by ASTM Subcommittee D19.06 to be ineffective.

8.3.6.3 Samples known or suspected to contain sulfide should be analyzed with an analytical test method that has been demonstrated to be free from sulfide interference. Test Method [D 6888](#) employs sulfide mitigation that can effectively remove up to 50 mg/L S^{2-} without prior treatment and has a lower method detection limit compared to colorimetric methods to compensate for any required dilutions specified in section [8.3.6.1](#). To determine total cyanide, distill as described in Test Methods [D 2036](#) Test Method A or equivalent method (for example, MIDI distillation described in [EPA 335.4](#)) and analyze the distillate by Test Method [D 6888](#) with sulfide abatement described in the method instead of colorimetry. Samples and distillates known or suspected to contain sulfide should be processed as quickly as possible to avoid cyanide degradation.

8.3.7 *Sulfite, Thiosulfate, or Thiocyanate*—Samples containing sulfite or thiosulfate can result in low cyanide recoveries when distilled. If thiocyanate is present, it can decompose into cyanide and sulfide during distillation. If sulfite, thiosulfate, or thiocyanate are known or suspected to be present, use a method that does not employ distillation and has been demonstrated to be free from these interferences. For available cyanide, use gas diffusion separation with amperometric detection (for example, Test Method [D 6888](#)), and for total cyanide use a UV digestion procedure (for example, Test Methods [D 4374](#) or Kelada-01). It is recommended to demonstrate that thiocyanate decomposition does not occur during the UV digestion by analyzing a prepared solution of SCN in water at the concentration suspected to be present in the sample(s).

8.3.8 *Sulfur*—To remove elemental sulfur (S_8), filter the sample immediately. If the filtration time will exceed 15 min, use a larger filter or a method that requires smaller sample volume. Adjust the pH of the filtrate to 12–13 with NaOH, refrigerate the filter and filtrate, then ship or transport to the laboratory.

TABLE 1 Examples of Potential Interferences in Standard Cyanide Methods

Method	Description	Measurement	Interferences	Number
Total Cyanide	Automated UV	Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity	CFR Kelada-01 D 4374
Total Cyanide	Manual Distillation MgCl ₂	Amperometric	Aldehydes Carbonates Fatty Acids Nitrite Nitrate Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate	D 2036 Test Method A
Total Cyanide	Manual Distillation MgCl ₂	Manual or Automated Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Color Turbidity	D 2036 Test Method A Standard Methods 4500-CN C/E, EPA 335.2, EPA 335.4
Total Cyanide	Manual Distillation MgCl ₂	ISE	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sulfide Sulfur Compounds Thiocyanate Color Turbidity	D 2036 Test Method A, Standard Methods 4500-CN C/F
Total Cyanide	Manual Distillation MgCl ₂	Titrimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D 2036 Test Method A, Standard Methods 4500-CN C/D
Available Cyanide	Flow Injection Ligand Exchange	Amperometric	Carbonates Oxidants Sulfide	D 6888, EPA OIA-1677
Cyanide Amenable to Chlorination	Alkaline Chlorination and Manual Distillations	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sulfide Sulfur Compounds Thiocyanate Color Turbidity Unknowns that cause negative results	D 2036 Test Method B, Standard Methods 4500-G/E

8.3.8.1 Extract the filter by shaking with 100 mL of 5 % NaOH solution for a minimum of 2 h. Filter the extract and discard the solids. Combine the 5 % NaOH-extracted filtrate

with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric acid or sulfuric acid, and analyze the