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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 addresses the mitigation of known interferences prior to the analysis of cyanide. Responsibilities of field sampling personnel and the laboratory are indicated.

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 [D2036](#), [D4282](#), [D4374](#), [D6888](#), [D6994](#), [D7237](#), [D7284](#), and [D7511](#). The information supplied in this practice can also be applied to other analytical methods for cyanide, for example, EPA Method 335.4.

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

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D2036 Test Methods for Cyanides in Water](#)
- [D3370 Practices for Sampling Water from Closed Conduits](#)
- [D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents](#)

- [D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water](#)
 - [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Methods for Cyanides in Water—Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate \(Withdrawn 2012\)³](#)
 - [D4411 Guide for Sampling Fluvial Sediment in Motion](#)
 - [D4840 Guide for Sample Chain-of-Custody Procedures](#)
 - [D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents](#)
 - [D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)
 - [D6888 Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis \(FIA\) Utilizing Gas Diffusion Separation and Amperometric Detection](#)
 - [D6994 Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection](#)
 - [D6696 Guide for Understanding Cyanide Species](#)
 - [D7237 Test Method for Free Cyanide with Flow Injection Analysis \(FIA\) Utilizing Gas Diffusion Separation and Amperometric Detection](#)
 - [D7284 Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection](#)
 - [D7511 Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection](#)
- ### 2.2 U.S. EPA Methods:⁴
- [EPA OIA-1677](#)
 - [EPA Method 335.2](#)
 - [EPA Method 335.4](#)

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

⁴ Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

2.3 USGS Methods:⁵

USGS I-3300-85

USGS I-4302-85

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this practice, refer to Terminology **D1129** and Guide **D6696**.

3.1.2 *refrigeration, n*—storing the sample between its freezing point and 6°C.

3.1.3 *holding time, n*—the time lapsed from sample collection to sample analysis.

4. Summary of Practice

4.1 Samples are collected in appropriate containers and mitigated for known interferences either in the field during sample collection or in the laboratory 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 **D1193**.

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 2 to 12. More than one test strip may be necessary to cover this range.

6.7 *Sodium Hydroxide Solution (1 M)*—In a 1-L volumetric flask, dissolve 40 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 *Ethylenediamine Solution (EDA), 3.5%*—Dilute 3.5 mL (or 3.15 g) of anhydrous $\text{NH}_2\text{CH}_2\text{NH}_2$ to 100 mL with water.

6.11 *Reducing Agents*—Ascorbic acid, sodium arsenite (NaAsO_2).

6.12 *Filter Paper or Syringe equipped with Leur-Lock Filters*—5 μm and 0.45 μm pore size. If unspecified, use 0.45 μm pore size.

6.13 *Dilute Acetic Acid*—Add 1 part glacial acetic acid to 9 parts water.

6.14 *Lead Carbonate (PbCO_3) or Lead Acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$)*, Lead acetate can be put in solution with water at a suggested concentration of 50 g/L.

6.15 *Sulfamic acid (0.4N), $\text{H}_2\text{NSO}_3\text{H}$* —Dissolve 40 g $\text{H}_2\text{NSO}_3\text{H}$ in 1 liter of water.

6.16 *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 **D3856**. When sampling closed conduits such as process streams refer to Practice **D3370**. When sampling fluvial sediment in motion or open channel flow refer to Guide **D4411**. It is recommended to consult with the analytical laboratory prior to collecting samples to ensure the proper sample volume, containers, etc., as these parameters may vary depending on the analytical methods used to measure the cyanide.

8.2 *Sample Containers:*

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

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 *Annual 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.

8.2.1 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 as well as rigid plastic containers made of high density polyethylene (HDPE) are suitable. Samples should be collected and stored in amber bottles to minimize exposure to ultraviolet radiation in the sample containers. If samples will only be tested for total cyanide, amber containers are not mandatory.

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 [D3694](#).

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 1 L is sufficient for most analytical test methods, however, flow injection and automated methods usually consume considerably less sample volume than manual methods.

8.3.2 Unless otherwise specified, samples must be analyzed within 14 days. Certain sample matrices may require a shorter holding time or immediate analysis to avoid cyanide degradation due to interferences. Hold the sample no longer than the time necessary to preclude a change in cyanide concentration. A holding time study described in Practice [D4841](#) is required if there is evidence that a change in cyanide occurs from interferences which would cause the holding time to be shorter than specified in this section, or within the time the sample would be held if shorter than the time specified in this section. Potential interferences and their corresponding analytical methods are shown in [Table 1](#).

NOTE 1—It is recommended to investigate holding times for samples that meet any of the following conditions—disinfected by chloramination or ultraviolet irradiation, ammonia present and chlorinated, sulfur dioxide or sulfite used to dechlorinate, or if aldehydes are known or suspected to be present.

8.3.3 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](#).

8.3.4 There may be interferences that are not mitigated by this procedure. Any technique for 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 or suppression technique not described in this practice or the analytical test method should be

documented along with supporting data. A challenge solution with potential interferences for cyanide analysis is described in [X1.1.1](#), which can be used as a sample matrix to examine analytical method performance.

8.3.5 Treat the sample immediately upon sample collection using any or all of the following techniques as necessary, followed by adjustment of the sample to pH > 10 and refrigeration. If applicable, laboratory mitigation techniques are also specified. Preserve the sample immediately (within 15 minutes of collection or treatment using procedures described in this practice) by adding 1 mL of 1M NaOH (Section [6.7](#)) per liter of sample, and then verify that the pH is greater than pH 10 with indicator test strips (Section [6.6](#)). If necessary, continue to add sodium hydroxide (Section [6.7](#) or [6.8](#)) drop wise until the pH is greater than pH 10 being careful not to add excess. Do not add NaOH if the cyanide concentration would change as a result of the addition.

8.3.5.1 Adding NaOH to samples containing formaldehyde (see [Note 2](#) in Section [8.3.8](#)) can possibly increase the cyanide concentration during storage. Conversely, adding NaOH to samples containing sulfite (see [Note 3](#) in Section [8.4.2.2](#)) can rapidly decrease the cyanide concentration. If the addition or lack of addition of NaOH would affect the holding time, hold the sample for a time no longer than the time necessary to maintain sample integrity (Section [8.3.2](#)).

8.3.6 *Sulfide*—During sample collection, 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 approximately 50 mg/L S²⁻) and treatment is necessary as described below.

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 S²⁻) or until the interference is no longer significant to the analytical test method. For example, add 50 mL of freshly collected sample into a bottle containing 200 mL of reagent water, then test for sulfide again with the lead acetate test strip. 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). It is recommended to perform this dilution during sample collection to avoid cyanide degradation; if this is not feasible, dilute the sample upon receipt in the laboratory and qualify the data. 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 Some analytical methods specify the use of lead carbonate or lead acetate to precipitate sulfide; however, sulfide and cyanide can form thiocyanate in the presence of lead sulfide causing decreased cyanide recoveries; therefore, lead carbonate and lead acetate should be avoided unless there is no other means to mitigate the sulfide or if the sample cannot be diluted as described in [8.3.6.1](#). Sulfide is removed by treating the sample with small increments of powdered lead carbonate

TABLE 1 Examples of Potential Interferences if not Mitigated in Standard Cyanide Methods

Method	Description	Measurement	Interferences	Number
Total Cyanide	Automated UV	Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity Sulfur Compounds Thiocyanate	CFR Kelada-01 D4374
Total Cyanide	Manual Distillation with H ₂ SO ₄ and MgCl ₂	Amperometric	Aldehydes Carbonates Nitrite Nitrate Oxidants Sulfide Sulfur Compounds Thiocyanate	D7284 D2036 Test Method A
Total Cyanide	Manual Distillation with H ₂ SO ₄ and MgCl ₂	Manual or Automated Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Color Turbidity	D2036 Test Method A EPA 335.2 EPA Method 335.2 , EPA 335.4
Total Cyanide	Manual Distillation with H ₂ SO ₄ and MgCl ₂	ISE	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sulfide Sulfur Compounds Thiocyanate Color Turbidity	D2036 Test Method A, Standard Methods 4500-CN C/F
Total Cyanide	Manual Distillation with H ₂ SO ₄ and MgCl ₂	Titrimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method A
Available Cyanide	Flow Injection Ligand Exchange	Amperometric	Carbonates Oxidants Sulfide	D6888 , 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	D2036 Test Method B

TABLE 1 *Continued*

Method	Description	Measurement	Interferences	Number
Weak Acid Dissociable Cyanide	Buffered Distillation	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method C
Weak Acid Dissociable Cyanide	Automated Method	Automated Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity	D4374
Weak Acid Dissociable Cyanide	Buffered Distillation	ISE	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method C
Weak Acid Dissociable Cyanide	Buffered Distillation	Titrimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D2036 Test Method C
Weak Acid Dissociable Cyanide	Buffered Distillation	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrite Nitrate Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Volatile Compounds	D2036 Test Method B
Metal Cyanide Complexes	Ion Chromatography	UV	Carbonate Dissolved Solids Metal Anions Metal Cations Oxidants Photodecomposition	D6994
Free Cyanide	Flow Injection	Amperometric	Carbonate Oxidants Sulfide	D7237
Free Cyanide	Microdiffusion	Colorimetric	Aldehydes Oxidants Sulfide Sulfur Compounds	D4282

TABLE 2 Potential Interferences with Selected Total Cyanide Methods Listed in 40 CFR Part 136

Methodology	Reference	Sample Processing	Determinative Step	Listed Interferences
Manual Distillation with Magnesium Chloride and Sulfuric Acid and Semi-Automated Colorimetry	EPA 335.4	The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution.	The cyanide ion in the absorbing solution is converted to CNCl by reaction with chloramine-T that subsequently reacts with pyridine and barbituric acid resulting in a red colored complex. The cyanide is determined with automated colorimetry.	(1) Oxidizing agents can destroy cyanides during storage. (2) Sulfide can complex with cyanide in sample or distillate. (3) Fatty acids cause interference during distillation. (4) Carbonate causes interference during distillation. (5) Aldehydes cause interference during distillation. (6) Glucose/Sugars cause interference during distillation. (7) Sulfur-containing compound causes interference during distillation by forming free sulfide that is captured in distillate. (8) Nitrate-Nitrite can cause high bias if sulfamic acid is not added during distillation
Manual Distillation with Magnesium Chloride and Sulfuric Acid	D2036 Test Method A	Total Cyanides is based on the decomposition of nearly all cyanides in the presence of strong acid, magnesium chloride catalyst, and heat during a 1-h reflux distillation.	Either the titration, colorimetric or selective ion electrode procedure can be used to quantify the cyanide concentration.	Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars, high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds.
Manual Distillation with Magnesium Chloride and Sulfuric Acid	USGS I-3300-85	The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences from water samples.	This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye.	Oxidizing agents may interfere. A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably. Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.
Cyanide by Automated Colorimetry	USGS I-4302-85	This method detects simple cyanides only; therefore, any complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.	This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent.	Oxidizing agents may interfere. A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably. Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.

or with the dropwise addition of lead acetate solution. Black lead sulfide precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with lead acetate test paper as indicated in 8.3.6. Immediately (within 15 minutes) filter with coarse filter paper (5 µm), then stabilize the sample according to 8.3.5. If the sample contains colloids that may contribute to

the total cyanide concentration, filter the sample prior to adding the lead, then recombine the solids with the filtrate prior to analysis. Samples that are known or suspected to contain sulfides should be analyzed as soon as possible to avoid cyanide degradation.

8.3.6.3 Precipitation of sulfide with cadmium chloride should be avoided since the formation of insoluble cadmium