~~Designation:D7365–07~~ Designation: D 7365 – 09

Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide[1]

This standard is issued under the fixed designation D 7365; 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 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. 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 D 2036, D 4282, D 4374, D 6888, D 6994~~, and D7237. This practice can also be applied to other cyanide methods, for example, US EPA Method 335.4 and Standard Methods 4500-CN C~~, D 7237, D 7284, and D 7511. 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]

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water ~~D1293Test 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 WaterAutomated 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 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

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~~ Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

[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.

~~Current edition approved Aug. 1, 2007. Published August 2007.~~

Current edition approved Feb. 15, 2009. Published March 2009. Originally approved in 2007. Last previous edition approved in 2007 as D 7365 – 07.

[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.

D 7284 Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection
D 7511 Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion 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*:
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

~~4.1Samples are collected in appropriate containers, mitigated for known interferences, and stabilized with sodium hydroxide prior to analysis.~~
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 D 1193.
6.3 *Acetate Buffer*— Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) 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~~2 to ~~14.~~12. More than one test strip may be necessary to cover this range.
6.7 *Sodium Hydroxide Solution ~~(5% wt/vol)~~(0.1 M)*—In a 1 L volumetric flask, dissolve ~~50~~4 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*— $Ca(OH)_2$ powder.

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[3] Available from United States Environmental Protection ~~Association~~Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://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.
[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For ~~s~~Suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Analar*~~*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.

6.10 ~~*Cadmium chloride*, $CdCl_2$.~~

~~6.11~~*Ethylenediamine (EDA)*

~~6.12~~

6.11 *Reducing Agents*~~— Sodium thiosulfate ($Na_2S_2O_3$), ascorbic acid, sodium arsenite ($NaAsO_2$), or sodium borohydride ($NaBH_4$)~~— Ascorbic acid, sodium arsenite ($NaAsO_2$).

~~6.13~~

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

~~6.14~~

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

~~6.15~~

6.14 *Sample Bottles*— See ~~section~~ 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*:

~~8.2.1Sample 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.~~

~~8.2.2Virgin 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~~

8.2.1 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 gas tight vials or narrow mouth bottles to minimize exposure to ultraviolet radiation and to minimize headspace in the sample containers (for example, amber open top VOA vials, amber Boston round bottles, or amber narrow-mouth HDPE bottles).

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.

~~8.2.3Samples 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 1 L is sufficient for most analytical test methods, however, flow injection and automated methods usually consume considerably less sample volume than manual methods.

~~8.3.2Certain 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 D4841. 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~~

8.3.2 Unless otherwise specified, samples must be analyzed within 14 days; however, it is recommended to estimate the actual holding time for each sample matrix as described in Practice D 4841. Certain sample matrices may require immediate analysis to avoid cyanide degradation due to interferences. A holding time study is required if there is evidence that cyanide degradation occurs from interferences which would cause the holding time to be less than specified in this practice. Potential interferences and their corresponding analytical methods are shown in Table 1.

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.

TABLE *Continued*

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	Automated UV	Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity Sulfur Compounds Thiocyanate	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 $MgCl_2$	Amperometric	Aldehydes Carbonates Nitrite Nitrate Oxidants Sulfide Sulfur Compounds Thiocyanate	D 7284 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

TABLE *Continued*

Method	Description	Measurement	Interferences	Number
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
Weak Acid Dissociable Cyanide	Buffered Distillation	Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D 2036 Test Method C, Standard Methods 4500-CN I/E
Weak Acid Dissociable Cyanide	Automated Method	Automated Colorimetric	Aldehydes Color Fatty Acids Mercury Nitrate Nitrite Oxidants Sulfides Turbidity	D 4374
Weak Acid Dissociable Cyanide	Buffered Distillation	ISE	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D 2036 Test Method C, Standard Methods 4500-CN I/F
Weak Acid Dissociable Cyanide	Buffered Distillation	Titrimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Turbidity	D 2036 Test Method C, Standard Methods 4500-CN I/D

TABLE *Continued*

Method	Description	Measurement	Interferences	Number
Weak Acid Dissociable Cyanide		Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrite Nitrate Oxidants Sugars Sulfide Sulfur Compounds Thiocyanate Volatile Compounds	D 2036 Test Method B, Standard Methods 4500-CN I/E
Metal Cyanide Complexes	Ion Chromatography	UV	Carbonate Dissolved Solids Metal Anions Metal Cations Oxidants Photodecomposition	D 6994
Free Cyanide	Flow Injection	Amperometric	Carbonate Oxidants Sulfide	D 7237
Free Cyanide	Microdiffusion	Colorimetric	Aldehydes Oxidants Sulfide Sulfur Compounds	D 4282