



Designation: D 7365 – 09

# Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide<sup>1</sup>

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 ( $\epsilon$ ) 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 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](#), [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:<sup>2</sup>

- [D 1129 Terminology Relating to Water](#)
- [D 1193 Specification for Reagent 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 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](#)
  - [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:<sup>3</sup>
- [EPA OIA-1677](#)
  - [EPA Method 335.2](#)
  - [EPA Method 335.4](#)
- ### 2.3 APHA Standard:<sup>4</sup>
- Standard Methods 4500-CN Methods C, D, E, F, G, and I
- ### 2.4 USGS Methods:<sup>5</sup>
- [USGS I-3300-85](#)

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

<sup>4</sup> 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](http://www.apha.org).

<sup>5</sup> Available from United States Geological Survey, 12201 Sunrise Valley Drive, Reston, VA, 20192, [www.usgs.gov](http://www.usgs.gov).

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

4.1 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.<sup>6</sup> 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  $\text{S}^{2-}$ .

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 (0.1 M)*—In a 1 L volumetric flask, dissolve 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*— $\text{Ca}(\text{OH})_2$  powder.

6.10 *Ethylenediamine (EDA)*

6.11 *Reducing Agents*—Ascorbic acid, sodium arsenite ( $\text{NaAsO}_2$ ).

6.12 *Filter Paper or Syringe equipped with Leur-Lock Filters*—Unless specified, 0.45  $\mu\text{m}$  pore size.

6.13 *Acidification Reagents*—Concentrated hydrochloric acid (HCl) or concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

6.14 *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, 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 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](#).

#### 8.3 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

<sup>6</sup> *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.

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; 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](#). 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 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 refrigeration. If applicable, laboratory mitigation techniques are also specified.

**NOTE 1**—Historically, sodium hydroxide has been added to preserve water samples for cyanide analysis during sample collection; however, this can result in rapid cyanide degradation or cyanide formation during sample storage. Therefore, sodium hydroxide should not be added as a preservative unless it is necessary to raise the pH for safety reasons (for example, process samples). If sodium hydroxide preservation is deemed necessary, add sodium hydroxide solution described in Sections [6.7](#) or [6.8](#) to pH 10–11, being careful not to add excess. Acidic samples (pH < 4) should be neutralized with sodium hydroxide solution upon sample collection.

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 S<sup>2-</sup>) 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 S<sup>2-</sup>) 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.

**NOTE 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 causing decreased cyanide recoveries; therefore, lead carbonate and lead acetate should be avoided unless there is no other means to mitigate the sulfide. If lead is used to remove sulfide, then the sample must be filtered immediately (within 15 minutes) to minimize the loss of cyanide. Precipitation with cadmium chloride should also be avoided since the formation of insoluble cadmium cyanide complexes can result in loss of cyanide. Sulfide volatilization techniques and 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.

8.3.6.2 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](#) optionally employs sulfide mitigation that can effectively remove up to 50 mg/L S<sup>2-</sup> 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 reduce or eliminate the need for dilution, samples containing up to 200 mg/L S<sup>2-</sup> can be analyzed for available cyanide within 24 hours using Test Method [D 6888](#) if the optional sulfide abatement reagent is prepared with 4 g/L bismuth nitrate pentahydrate in 1 M H<sub>2</sub>SO<sub>4</sub> instead of 1 g/L as described in the test method. Since sulfide competes with cyanide in the reaction with colorimetric methods, it is recommended to determine total cyanide with Test Methods [D 7284](#), [D 7511](#), or distill as described in Test Methods [D 2036](#) Test Method A or equivalent method (for example, MIDI distillation described in [EPA Method 335.4](#)) then analyze the distillate by Test Method [D 6888](#) with sulfide abatement. Alternatively, Test Method [D 4374](#) specifies that up to 10 mg/L S<sup>2-</sup> can be tolerated without significant interference. Samples and distillates known or suspected to contain sulfide should be processed as quickly as possible to avoid cyanide degradation.

8.3.7 *Sulfur*—To remove elemental sulfur (S<sub>8</sub>), filter the sample immediately upon sample collection. If the filtration time will exceed 15 min, use a larger filter or a method that requires smaller sample volume. Syringe filters may be used for methods that do not require large sample volume. Do not use vacuum filtration as this may cause cyanide loss. If the sample contains a significant amount of particulate matter (for example, >1 % suspended solids) or if the sample is known or suspected to contain particulate cyanides (for example, ferric

**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 D 4374
Total Cyanide	Manual Distillation MgCl <sub>2</sub>	Amperometric	Aldehydes Carbonates Nitrite Nitrate Oxidants Sulfide Sulfur Compounds Thiocyanate	D 7284 D 2036 Test Method A
Total Cyanide	Manual Distillation MgCl <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub>	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

**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	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
Weak Acid Dissociable Cyanide		Manual Colorimetric	Aldehydes Carbonates Fatty Acids Nitrate Nitrite 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



**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	SM 4500 CN E	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.	Cyanide in the alkaline distillate from preliminary treatment is converted to CNCl by reaction with chloramine-T at pH < 8 without hydrolyzing to CNO-. After reaction, CNCl forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color absorbance in aqueous solution is between 575 and 582 nm.	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	SM 4500-CN D	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.	Cyanide in the alkaline distillate from the preliminary treatment procedure (4500-CN-B) is titrated with standard silver nitrate (AgNO <sub>3</sub> ) to form the soluble cyanide complex, Ag(CN) <sup>2-</sup> . As soon as all CN <sup>-</sup> has been complexed and a small excess of Ag <sup>+</sup> has been added, the excess Ag <sup>+</sup> is detected by the silver-sensitive indicator, p-dimethylaminobenzalrhodanine, which immediately turns from a yellow to a salmon color. The distillation has provided a 2:1 concentration. The indicator is sensitive to about 0.1 mg Ag/L.	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	D 2036 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.

ferro cyanide or Prussian blue), save the solids for extraction as described in Section 8.4.3 on particulate cyanides, otherwise, discard the solids and filter.

8.3.8 *Aldehydes*—If formaldehyde, acetaldehyde, or other water-soluble aldehydes are known or suspected to be present,

treat the sample with 20 mL 3.5 % ethylenediamine per L of sample to avoid the formation of cyanohydrins. Samples can be screened for the presence of formaldehyde and other water-soluble aldehydes using test strips for formaldehyde or aldehydes.