Designation: D2036 – 09

Standard Test Methods for Cyanides in Water[1]

This standard is issued under the fixed designation D2036; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover the determination of cyanides in water. The following test methods are included:

	Sections
Test Method A—Total Cyanides after Distillation	12 to 18
Test Method B—Cyanides Amenable to Chlorination[2] by Difference	19 to 25
Test Method C—Weak Acid Dissociable Cyanides	26 to 32
Test Method D—Cyanides Amenable to Chlorination without Distillation (Short-Cut Method)	33 to 39

1.2 Cyanogen halides may be determined separately.

NOTE 1—Cyanogen chloride is the most common of the cyanogen halide complexes as it is a reaction product and is usually present when chlorinating cyanide-containing industrial waste water. For the presence or absence of CNCl, the spot test method given in Annex A1 can be used.

1.3 These test methods do not distinguish between cyanide ions and metallocyanide compounds and complexes. Furthermore, they do not detect the cyanates. Cyanates can be determined using ion chromatography without digestion.

NOTE 2—The cyanate complexes are decomposed when the sample is acidified in the distillation procedure.

1.4 The cyanide in cyanocomplexes of gold, platinum, cobalt and some other transition metals is not completely recovered by these test methods. Refer to Test Method D6994 for the determination of cyanometal complexes.

1.5 Cyanide from only a few organic cyanides are recovered, and those only to a minor extent.

1.6 Part or all of these test methods have been used successfully with reagent water and various waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

1.7 *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.* Specific hazard statements are given in sections 5.1, 8.8, 8.18, 9, 11.3, and 16.1.9.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D5788 Guide for Spiking Organics into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6696 Guide for Understanding Cyanide Species
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
D7284 Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection
D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide
D7511 Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] For an explanation of the term cyanides amenable to alkaline chlorination, see Lancy, L. E. and Zabban, W., "Analytical Methods and Instrumentation for Determining Cyanogen Compounds," *Papers on Industrial Water and Industrial Waste Water, ASTM STP 337*, 1962, pp. 32–45.

[3] 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.

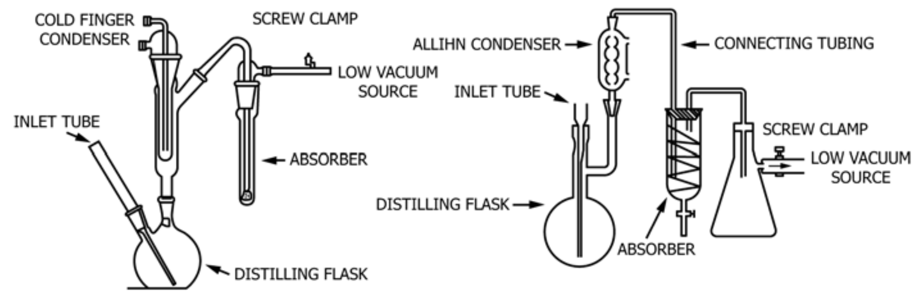

FIG. 1 Cyanide Distillation Apparatus

3. Terminology

3.1 *Defenitions*—For definitions of terms used in these test methods, refer to Terminology D1129 and Guide D6696.

3.2 *Acronyms:*

3.2.1 *HPLC, n*—high performance liquid chromatography

3.2.2 *IC, n*—ion chromatography

3.2.3 *PAD, n*—pulsed amperometric detection

3.2.4 *FIA, n*—flow injection analysis

4. Summary of Test Methods

4.1 The cyanide as hydrocyanic acid (HCN) is released from compounds by means of reflux distillation and absorbed in sodium hydroxide solution. The conditions used for the distillation distinguish the type of cyanide. The sodium cyanide in the absorbing solution can be determined colorimetrically, by ion chromatography, titration, by selective ion electrode, or as described in Test Method D6888 using flow injection with amperometric detection.

4.2 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.

4.3 Test Method B, Cyanide Amenable to Chlorination, is based on chlorinating a portion of the sample under controlled conditions followed by the determination of total cyanide in both the original and chlorinated samples. Cyanides amenable to chlorination are calculated by difference.

4.3.1 This test method can be affected by compounds that are converted during chlorination to color-producing compounds or react with the reagents used, and cause interference in the procedure employed to determine cyanide in the absorption solution.

4.4 Test Method C, Weak Acid Dissociable Cyanides, is based on the decomposition of cyanides in the presence of weak acid, zinc acetate and heat during a 1-h reflux distillation.

4.5 Test Method D, Cyanide Amenable to Chlorination without Distillation, is a direct colorimetric procedure.

4.6 In the absence of interference, the minimum concentration of cyanide in the absorption solution that can be accurately determined colorimetrically is 0.005 mg/L, ion chromatography and Test Method D6888 are 0.002 mg/L, titration is 0.4 mg/L and by selective ion electrode is 0.05 mg/L. Pretreatment including distillation tends to increase these concentrations to a degree determined by the amount of manipulation required and the type of sample.

4.7 Round-robin data indicate the following minimum concentrations: colorimetric 0.03 mg/L; titration 1.0 mg/L; and selective ion electrode 0.03 mg/L. Ion chromatography and Test Method D6888 have a minimum levels equal to approximately 0.002 mg/L.

5. Significance and Use

5.1 Cyanide is highly toxic. Regulations have been established to require the monitoring of cyanide in industrial and domestic wastes and in surface waters (Appendix X1).

5.2 Test Method D is applicable for natural water and clean metal finishing or heat treatment effluents. It may be used for process control in wastewater treatment facilities providing its applicability has been validated by Test Method B or C.

5.3 The spot test outlined in Annex A1 can be used to detect cyanide and thiocyanate in water or wastewater, and to approximate its concentration.

6. Interferences

6.1 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.

6.2 It is beyond the scope of these test methods to describe procedures for overcoming all of the possible interferences that may be encountered. Refer to Practice D7365 for potential interferences for the analysis of cyanide in water.

7. Apparatus

7.1 *Distillation Apparatus*—The reaction vessel shall be a 1-L round bottom flask, with provision for an inlet tube and a condenser. The inlet tube shall be a funnel with an 8-mm diameter stem that extends to within 6 mm of the bottom of the flask. The condenser, which is recommended, shall be a reflux-type, cold finger, or Allihn. The condenser shall be connected to a vacuum-type absorber which shall be in turn connected to a vacuum line which has provision for fine control. The flask shall be heated with an electric heater. Examples of the apparatus are shown in Fig. 1. Equivalent apparatus is acceptable provided cyanide recoveries of 100 ± 4 % are documented.

7.1.1 Smaller distillation tubes such as 50-mL MIDI tubes or 6-mL MicroDist (trademarked) tubes described in Test

Method D7284 can be used if the quality control requirements in Section 40 are satisfied. The reagents should be added proportionately to those specified in this test method for smaller sample sizes. While the use of smaller distillation tubes is generally accepted, the interlaboratory study was conducted with 500-mL samples; therefore, the user is responsible to determine the actual precision and bias when using a different type of distillation apparatus.

7.2 *Spectrophotometer or Filter Photometer,* suitable for measurement in the region of 578 nm, using 1.0-, 2.0-, 5.0-, and 10.0-cm absorption cells. Filter photometers and photometric practices used in these test methods shall conform to Practice E60. Spectrophotometers shall conform to Practice E275.

7.3 *Selective Ion Meter,* or a pH meter with expanded millivolt scale equipped with a cyanide activity electrode and a reference electrode.

7.4 *Mixer,* magnetic, with a TFE-fluorocarbon-coated stirring bar.

7.5 *Buret,* Koch, micro, 2- or 5-mL, calibrated in 0.01 mL.

7.6 *Ion Chromatograph*, high performance ion chromatograph equipped with a 10-µL sample injection device and pulsed-amperometric detector.

7.7 *Chromatography Column*, Dionex IonPac AS7 anion-exchange, 4 × 250 mm and matching guard column or equivalent.

8. Reagents and Materials

8.1 *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, where such specifications are available.[4] 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.

8.2 *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.

8.3 *Acetic Acid* (1 + 9) —Mix 1 volume of glacial acetic acid with 9 volumes of water.

8.4 *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.

8.5 *Barbituric Acid.*

8.6 *Calcium Hypochlorite Solution* (50 g/L)—Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 mL of water. Store the solution in an amber glass bottle in the dark. Prepare fresh monthly.

8.7 *Chloramine-T Solution* (10 g/L)—Dissolve 1.0 g of the white-colored, water-soluble grade powder chloramine-T in 100 mL of water. Prepare fresh weekly.

8.8 *Cyanide Solution, Stock* (1 mL = 250 µg CN^-)—Dissolve 0.6258 g of potassium cyanide (KCN) in 40 mL of sodium hydroxide solution (40 g/L). Dilute to 1 L with water. Mix thoroughly. Standardize with standard silver nitrate solution following the titration procedure (see 16.2). (**Warning—**Because KCN is highly toxic, avoid contact or inhalation (see 9)). Commercial solutions may also be used if certified by the manufacturer and used within the recommended storage date.

8.8.1 *Cyanide I Solution, Standard* (1 mL = 25 µg CN^-)—Dilute a calculated volume (approximately 100 mL) of KCN stock solution to 1 L with NaOH solution (1.6 g/L).

8.8.2 *Cyanide II Solution, Standard* (1 mL = 2.5 µg CN^-)—Dilute exactly 100 mL of KCN standard solution I to 1 L with NaOH solution (1.6 g/L).

8.8.3 *Cyanide III Solution, Standard* (1 mL = 0.25 µg CN^-)— Dilute exactly 100 mL of KCN standard solution II to 1 L with NaOH solution (1.6 g/L). Prepare fresh solution daily and protect from light.

8.8.4 *Cyanide IV Solution, Standard* (1 mL = 0.025 µg CN^-)— Dilute exactly 100 mL of KCN standard solution III to 1 L with NaOH solution (1.6 g/L). Prepare fresh solution daily and protect from light.

8.9 *Hydrogen Peroxide Solution*, 3 %—Dilute 10 mL of 30 % hydrogen peroxide (H_2O_2) to 100 mL. Prepare fresh weekly.

8.10 *Isooctane, Hexane, Chloroform* (solvent preference in the order named).

8.11 *Lead Carbonate* ($PbCO_3$), *Lead Acetate* ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$), or *Lead Nitrate* ($Pb(NO_3)_2$)—Lead acetate and lead nitrate can be put in solution with water, if desired, at a suggested concentration of 50 g/L.

8.12 *Lime,* hydrate ($Ca(OH)_2$), powder.

8.13 *Magnesium Chloride Solution*—Dissolve 510 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) in water and dilute to 1 L.

8.14 *Potassium Iodide-Starch Test Paper.*

8.15 *Pyridine-Barbituric Acid Reagent*—Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of hydrochloric acid (sp gr 1.19), mix, and cool to room temperature. Dilute to volume with water and mix until all of the barbituric acid is dissolved. This solution is usable for about 6 months if stored in a cold dark place. Commercially prepared solutions may be available; follow the manufacturer's expiration date.

8.16 *Rhodanine Indicator Solution* (0.2 g/L)—Dissolve 0.02 g of (p-dimethylaminobenzylidene) in 100 mL of acetone.

8.17 *Silver Nitrate Solution, Standard* (0.01 *N*)—Dissolve 1.6987 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

[4] *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.

Mix thoroughly. Commerical solutions that are certified at the designated normality are suitable if used within the manufacturer's recommended storage date. Store in a dark container.

8.18 *Sodium Arsenite Solution* (20 g/L)—Dissolve 2 g of $NaAsO_2$ in 100 mL of water. **Warning—**This material has appeared on lists of suspected and known carcinogens. Avoid contact with skin.

8.19 *Sodium Hydroxide Solution* (40 g/L)—Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 1 L with water.

8.20 *Sodium Hydroxide Solution* (1.6 g/L)—Dilute 40 mL of NaOH solution (40 g/L) to 1 L.

8.21 *Sulfamic Acid Solution* (133 g/L)—Dissolve 133 g of sulfamic acid in water and dilute to 1 L.

8.22 *Sodium Thiosulfate Solution* (500 g/L)—Dissolve 785 g of sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$) in water and dilute to 1 L.

8.23 *Sulfuric Acid* (1 + 1) —Slowly and carefully add 1 volume of sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water, stirring and cooling the solution during the addition.

8.24 *Zinc Acetate Solution* (100 g/L)—Dissolve 120 g of zinc acetate [$Zn(C_2H_3O_2)_2{\cdot}2H_2$] in 500 mL of water. Dilute to 1 L.

8.25 *IC Eluent Solutions,* (75 mM sodium hydroxide, 250 mM sodium acetate, and 0.05 % (v/v) ethylenediamine)

8.25.1 *Eluent Preparation*—Weigh 20.50 g of anhydrous NaOAc and dissolve it in 500–600 g of 18 MΩ-cm water. Fill up to ~980 g with 18 MΩ-cm water. Stir thoroughly and filter through a 0.2 µm Nylon filter. Add 5.97 g (3.9 mL) of 50 % NaOH and 0.4495 g (0.50 mL) of ethylendiamine. Fill up to 1015 g (1.0 L) with 18 MΩ-cm water in the bottom container of the filtration unit. Transfer the solution immediately to the eluent container, which is connected to nitrogen. Adjust the flow rate at 0.25 mL/min (for a 2-mm ID column) or 1.00 mL/min (for a 4-mm ID column)

8.26 *Ethylene diamine.*

8.27 *Sodium Hydroxide Solution (50 % W/W)*. It is essential to use high quality 50 % (w/w) sodium hydroxide solution for eluent and diluent preparation for use in ion chromatography. Sodium hydroxide pellets are coated with sodium carbonate and, therefore, are not acceptable for this application.

8.28 *Sodium Acetate.*

9. Hazards

9.1 **Warning—**Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). All manipulations must be done in the hood so that any HCN gas that might escape is safely vented.

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

9.3 All reagents and standards should be prepared in volumes consistent with laboratory use to minimize the generation of waste.

10. Sample and Sample Preservation

10.1 Collect the sample in accordance with Practice D7365. This standard practice is applicable for the collection and preservation of water samples for the analysis of cyanide. Responsibilities of field sampling personnel and the laboratory are indicated.

11. Elimination of Interferences

11.1 Refer to Practice D7365 for mitigating interferences for the analysis of cyanide in water.

11.2 The following treatments are specific for the removal or reduction of substances that can interfere in the various methods of this test method. Care must be taken to keep time of pretreatment at a minimum to avoid loss of cyanide.

11.3 Fatty acids that distill and form soaps in the absorption solution can be removed by extraction. Acidify the sample with dilute (1 + 9) acetic acid to a pH 6 to 7 (perform this operation in the hood and leave the sample there until it is made alkaline after the extraction). Extract with *iso*octane, hexane or chloroform (preference in order named), with a solvent volume equal to 20 % of the sample volume. One extraction is usually sufficient to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN to a minimum. When the extraction is complete, immediately raise the pH of the sample to 12 to 12.5 with NaOH solution.

11.4 Aldehydes combine with cyanides to form cyanohydrins which can hydrolyze to acids under distillation conditions. Glucose and other sugars, if present in the sample, can also form cyanohydrins with cyanide at the pH of preservation. Aldehydes can be removed as described in Practice D7365.

11.5 Carbonate in high concentration can affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when acid is added prior to distillation, and by lowering the pH of the absorption solution.

11.6 Nitrite and nitrate in the sample can react under conditions of the distillation with other contaminants present to form cyanides. The addition of an excess of sulfamic acid to the sample prior to the addition of sulfuric acid will reduce this interference. For example, if samples are known or suspected to contain nitrate or nitrite, add 50 mL of 0.4 N sulfamic acid solution (40 g/L) per 500 mL sample, then proceed with distillation after 3 minutes.

11.7 Thiocyanate and other sulfur containing compounds can decompose during distillation. Sulfur, hydrogen sulfide, sulfur dioxide, etc., formed can be distilled into the absorption solution. The addition of lead ion to the absorption solution before distillation followed by filtration of the solution before the titration or the colorimetric procedure is used will minimize sulfur and sulfide interference. Absorbed sulfur dioxide forms sodium sulfite which reacts with chloramine-T in the colorimetric determination. Test for the presence of chloramine-T by placing a drop of solution on a strip of potassium iodide test paper previously moistened with dilute acetic acid. If the test is negative, add chloramine-T until a positive test is obtained.

11.7.1 Cyanide can be measured in the presence of sulfur containing compounds by using IC to separate the interferences from the cyanide (16.5). Samples or distillates containing up to 50 mg/L sulfide can be analyzed with sulfide abatement acidification reagent as described in Test Method D6888.

11.7.2 False positive results have been observed for total cyanide in samples containing thiocyanate in the presence of ammonia and nitrate. To avoid this interference, use a method that does not require distillation such as Test Method D6888. Adding 0.6 g/L ascorbic acid prior to distillation may also reduce the interference; treated samples should be analyzed within 24 hours.

11.7.3 Separation of the cyanide from interfering substances prior to electrochemical determination (see 16.5 for ion chromatography procedure) should be conducted when using Test Method A—Total Cyanides After Distillation, or Test Method B—Cyanides Amenable to Chlorination by the Difference when sulfur, thiocyanate, or other sulfur containing compounds are present.

11.8 Thiocyanate in the presence of ferric ion is quantitatively determined by the colorimetric procedure. Test Method D outlines a procedure for masking any cyanide amenable to chlorination in order to determine thiocyanate by difference.

11.9 Substances which contribute color or turbidity interfere with Test Method D.

TEST METHOD A—TOTAL CYANIDES AFTER DISTILLATION

12. Scope

12.1 This test method covers the determination of cyanides in water, including the iron cyanide complexes (total cyanide).

12.2 The cyanide in some cyano complexes of transition metals, for example, cobalt, gold, platinum, etc., is not determined.

12.3 The cyanide concentration can be determined with titration, IC-PAD, colorimetric, selective ion electrode procedure, or flow injection analysis with gas diffusion separation and amperometric detection as described in Test Method D6888.

12.4 This test method has been used successfully on reagent and surface water and coke plant, refinery, and sanitary waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

12.5 Because of the sample preservation, certain suspended and/or colloidal forms of metal cyanide complexes such as those from iron and copper will dissolve prior to the distillation step. The recovery of this cyanide may depend on solution parameters such as the cyanide concentration in suspended solids, ionic strength of the sample, sample temperature, acid digestion times, and so forth.

13. Interferences

13.1 All the chemical compounds listed in Section 6 can interfere.

13.2 For the removal of these interferences, proceed as instructed in Sections 10 and 11.

14. Apparatus

14.1 The schematic arrangement of the distillation system is shown in Fig. 1.

14.2 For the required apparatus, refer to Section 7.

15. Reagents and Materials

15.1 Refer to Section 8.

16. Procedure

16.1 *Distillation Procedure:*

16.1.1 Set up the apparatus as shown in Fig. 1.

16.1.2 Add 10.0 mL of 1 M NaOH solution to the absorber. Dilute with water to obtain an adequate depth of liquid. Do not use more than 225 mL of total volume in the absorber.

16.1.3 Attach the absorber to the vacuum and connect to the condenser.

16.1.4 Place 500 mL of the sample in the flask. If cyanide content is suspected to be more than 10 mg/L, use an aliquot so that no more than 5 mg of cyanide is in the distilling flask and dilute to 500 mL with water. Annex A1 describes a procedure for establishing the approximate cyanide content. Verify a negative reaction in the spot-plate technique by using 500 mL of the sample.

16.1.5 Connect the flask to the condenser.

16.1.6 Turn on the vacuum and adjust the air flow to approximately 1 bubble per second entering the boiling flask through the air-inlet tube.

16.1.7 Add 20 mL of magnesium chloride solution (8.13) through the air inlet tube. If the sample contains nitrite or nitrate, add 15 mL of sulfamic acid solution (8.21).

16.1.8 Rinse the air-inlet tube with a few mL of water and allow the air flow to mix the content of the flask for approximately 3 min.

16.1.9 Carefully add 50 mL of H_2SO_4 solution (1 + 1) through the air-inlet tube. (**Warning—** Add slowly; heat is generated and foaming may occur.)

16.1.10 Turn on the condenser cooling water. Heat the solution to boiling, taking care to prevent the solution from backing into the air-inlet tube.

16.1.11 Maintain the air flow as in 16.1.6.

16.1.12 Reflux for 1 h.

16.1.13 Turn off the heat, but maintain the air flow for at least an additional 15 min.

16.1.14 For 500-mL macro distillations, quantitatively transfer the absorption solution into a 250-mL volumetric flask. Rinse absorber and its connecting tubes sparingly with water and add to the volumetric flask.

16.1.15 Dilute to volume with water and mix thoroughly.

16.1.16 Determine the concentration of cyanide in the absorption solution by one of the procedures—titration (Section 16.2), colorimetric (16.3), selective ion electrode (16.4), ion chromatography (16.5), or flow injection with gas diffusion separation with amperometric detection as described in Test

TABLE 1 Guide for Selection of Appropriate Cell Paths

Standard Solution No.	Millitres of Standard Solution	Final Concentration, µg CN/mL	Cell Length, cm		
	50 mL		1.0	5.0	10.0
IV	5.0	0.0025			X
IV	10.0	0.0050		X	X
IV	15.0	0.0075		X	X
IV	20.0	0.0100		X	X
IV	25.0	0.0125		X	X
IV	30.0	0.0150		X	X
IV	40.0	0.0200		X	
III	5.0	0.0250	X	X	
III	10.0	0.0500	X		
III	15.0	0.0750	X		
III	20.0	0.1000	X		
III	25.0	0.1250	X		
III	30.0	0.1500	X		
	0.0 (blank)		X	X	X

Method D6888 (16.6). See Sections 4.6 and 4.7 for minimum concentration levels for each procedure prior to choosing a determinative step.

16.2 *Titration Procedure:*

16.2.1 Place 100 mL of the absorption solution or an accurately measured aliquot diluted to 100 mL with NaOH solution (1.6 g/L) in a flask or beaker.

16.2.2 Add 0.5 mL of rhodanine indicator solution.

16.2.3 Titrate with standard silver nitrate solution (8.17) using a microburet to the first change from yellow to salmon pink.

16.2.4 Titrate a blank of 100 mL of NaOH solution (1.6 g/L) (8.20).

16.2.5 Record the results of the titration and calculate the cyanide concentration in the original samples according to Eq 1 (17.1).

16.3 *Colorimetric Procedure:*

16.3.1 *Standardization:*

16.3.1.1 Prepare a series of cyanide standards based on the cell path which is used (Table 1). For this purpose use 50-mL glass-stoppered volumetric flasks or graduated cylinders.

16.3.1.2 Follow 16.3.2.2 through 16.3.2.6 of the procedure.

16.3.1.3 Calculate the absorption factor (17.2.1).

16.3.2 *Procedure:*

16.3.2.1 Pipet an aliquot of the absorption liquid, such that the concentration falls within the standardization range, into a 50-mL glass-stoppered volumetric flask or graduated cylinder.

16.3.2.2 If necessary, dilute to 40 mL with the NaOH solution used in the absorber solution.

16.3.2.3 Place 40 mL of the NaOH solution used in the absorber solutions in a flask or cylinder for a blank. (Carry out the following steps of the procedure on the blank also.)

16.3.2.4 Add 1 mL of chloramine-T solution and 1 mL of acetate buffer, stopper, mix by inversion two or three times, and allow to stand for exactly 2 min.

16.3.2.5 Add 5 mL of pyridine-barbituric acid reagent, dilute to volume with water, mix thoroughly, and allow to stand exactly 8 min for color development.

16.3.2.6 Measure at the absorbance maximum at 578 nm. Measure absorbance (*A*) versus water.

16.3.2.7 Calculate the concentration of cyanide (mg CN/L) in the original sample following equations given in 17.2.

16.4 *Selective Ion Electrode Procedure:*

16.4.1 *Standardization:*

16.4.1.1 Place 100-mL aliquots of standard solutions I, II, III, and IV in 250-mL beakers.

16.4.1.2 Follow 16.4.2.2 and 16.4.2.3.

16.4.1.3 Pipet 10- and 50-mL aliquots of standard solution IV into 250-mL beakers and dilute to 100 mL with NaOH solution (1.6 g/L).

16.4.1.4 Follow 16.4.2.2 and 16.4.2.3 of the procedure, starting with the lowest concentration.

16.4.1.5 Plot concentration values of the standardizing solutions on the logarithmic axis of semilogarithmic graph paper versus the potentials developed in the standardizing solutions on the linear axis. Follow manufacturer's instructions for direct-reading ion meters.

16.4.2 *Procedure:*

16.4.2.1 Place 100 mL of the absorption solution (or an accurately measured aliquot diluted to 100 mL with NaOH solution (1.6 g/L)) in a 250-mL beaker.

NOTE 3—Check a small portion of the solution for sulfide. If it is present, add either the $PbCO_3$ or $Pb(C_2H_3O_2)_2$ immediately before inserting the electrodes.

16.4.2.2 Place the beaker on a magnetic stirrer, place a TFE-fluorocarbon-coated stirring bar in the solution, stir at a predetermined constant rate, and maintain constant temperature.

16.4.2.3 Insert the cyanide specific ion electrode and the reference electrode in the solution and measure potential or the cyanide concentration following the manufacturer's instructions.

16.4.2.4 Use values found from the graph or direct-reading ion meter to calculate the concentration in the original sample following Eq 5 (17.3).

16.5 *Ion Chromatography Procedure:*

16.5.1 *Standardization:*

16.5.1.1 Place 2-mL of standard solutions I, II, III, and IV into HPLC autosampler vials if using an autosampler, or other capped glass vial if using a manual injector.

16.5.1.2 Follow 16.5.2.1 through 16.5.2.4 to standardize the IC detector response by injection of 10 µL of each standard solution.

NOTE 4—A 10-µL injection was used for the interlaboratory study. Other levels can be used provided the analyst confirms the precision and bias is equivalent with that generated using the 10-µL injection.

16.5.1.3 Measure the area under the cyanide peak. This is the detector response.

16.5.1.4 Plot concentration values of the standard solution versus detector response. Follow manufacturer's instruction for IC systems with computer controlled data stations.

16.5.2 *Procedure:*

16.5.2.1 Set the ion chromatograph to operate at the following conditions or as required for instrument being used:

(*a*) *Flow Rate*: 1.0 mL/min.

(*b*) *PAD* operated in a dc amperometric mode with a silver-working-electrode set at –0.05 V in relation to a standard

TABLE 2 Waveform for Analysis of Cyanide by Ion Chromatography

Time (sec)	Potential (V) vs. Ag/AgCl, 3 M KCl	Integration
0.00	–0.10	-
0.20	–0.10	Start
0.90	–0.10	End
0.91	–1.00	-
0.93	–0.30	-
1.00	–0.30	-

Ag/AgCl-reference electrode or an equivalent detector. Other working electrodes such as platinum or boron-doped diamond electrodes have also been shown to be effective. Optimize the waveform based on the electrode used.

(c) Column, Dionex IonPac AS 7 anion-exchange, 4 × 250 mm and matching guard column or equivalent.

(d) Temperature: Ambient.

(e) Sample size: 10 µL.

16.5.2.2 Prime the IC pump and ensure that the flow rate is 1.0 mL/min. Allow the detector to warm up for 30-60 min to stabilize the baseline.

16.5.2.3 Inject 10-µL of sample solution into the IC system. Apply the waveform from Table 2. A 10-µL injection of 50 ppb standard of cyanide should result in a well-defined peak with an area >1.0 nC min and with asymmetry in the range of 0.9 to 2.0 for 2-mm ID column set. With a 4-mm ID column set a 50-µL injection of the same standard should generate a peak area >0.8 nC min in the same range of asymmetry values.

16.5.2.4 Use values found from the graph or data station to calculate the concentration in the original sample following Eq 5 (17.3).

16.6 *Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection Procedure:*

16.6.1 For total cyanide, test the sample distillates with Test Method D6888.

17. Calculation

17.1 *Titration Procedure*—Calculate the concentration in milligrams of CN per litre in the original sample using Eq 1:

$$\text{mg CN/L} = [(A - B) \times N \text{ AgNO}_3 \times 0.052/\text{mL original sample}] \times (250/\text{mL aliquot used}) \times 10^{6} \quad (1)$$

where:

A = $AgNO_3$ solution to titrate sample, mL, and
B = $AgNO_3$ solution to titrate blank, mL.

17.2 *Colorimetric Procedure*—Calculate the concentration in milligrams of CN per litre as follows:

17.2.1 *Slope and Intercept of Standard Curve*—Calculate the slope on the standard curve, m, and the intercept on c-axis, b, using Eq 2 and Eq 3, respectively:

$$m = \frac{n\sum ca - \sum c \sum a}{n\sum a^{2} - \left(\sum a\right)^{2}} \quad (2)$$

$$b = \frac{\sum a^{2} \sum c - \sum a \sum ac}{n\sum a^{2} - \left(\sum a\right)^{2}} \quad (3)$$

where:

a = absorbance of standard solution,
c = concentration of CN^- in standard, mg/L, and
n = number of standard solutions.

17.2.1.1 the blank concentration, 0.0 mg CN^- /L, and the absorbance of the blank must be included in the calculation of slope and intercept.

17.2.2 *Concentration*—Calculate the concentration of cyanides using Eq 4:

$$\text{CN, mg/L} = (ma_1 + b)\ X\ \frac{40}{X}\ X\ \frac{250}{Y} \quad (4)$$

where:

a_1 = absorbance of sample solution,
X = aliquot of absorbance solution, mL, and
Y = original sample, mL.

17.3 *Selective-Ion Electrode and Ion Chromatography Procedures*—Calculate the concentration in milligrams of CN per litre using Eq 5:

$$\text{CN, mg/L} = \text{CN mg/L from graph or meter} \times (100/\text{aliquot}) \times (250/\text{mL original sample}) \quad (5)$$

18. Precision and Bias[5]

18.1 *Precision:* All methods have met the requirements for Practice D2777 for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water.

18.1.1 *Colorimetric*—Based on the results of nine operators in nine laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	$S_T = 0.06x + 0.003$
	$S_o = 0.11x + 0.010$
Selected Water Matrices	$S_T = 0.04x + 0.018$
	$S_o = 0.04x + 0.008$

18.1.2 *Electrode*—Based on the results of six operators in five laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	$S_T = 0.06x + 0.003$
	$S_o = 0.03x + 0.008$
Selected Water Matrices	$S_T = 0.05x + 0.008$
	$S_o = 0.03x + 0.012$

18.1.3 *Titrimetric*—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	$S_T = 0.04x + 0.038$
	$S_o = 0.01x + 0.018$
Selected Water Matrices	$S_T = 0.06x + 0.711$
	$S_o = 0.04x + 0.027$

18.1.4 *Ion Chromatography Procedure*—The precision was determined in accordance with Practice D2777. Based on the results of eight operators in eight laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:D19-1131.

TABLE 3 Reagent Water (Test Method A)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	%Bias	Statistical Significance, 95 % CL
Colorimetric	0.060	0.060	26	0.0101	0.000	0	No
	0.500	0.480	23	0.0258	−0.020	−4	No
	0.900	0.996	27	0.0669	0.096	11	Yes
Electrode	0.060	0.059	18	0.0086	−0.001	2	No
	0.500	0.459	18	0.0281	−0.041	−8	Yes
	0.900	0.911	18	0.0552	0.011	1	No
	5.00	5.07	18	0.297	0.07	1	No
Titrimetric	2.00	2.10	18	0.1267	0.10	5	Yes
	5.00	4.65	18	0.2199	−0.35	−7	Yes
	5.00	5.18	18	0.2612	0.18	4	Yes

$$\text{xbar} = 1.04x + 0.35$$

$$S_T = 0.057x + 3.19$$

$$S_o = 0.020x + 3.90$$

18.1.5 A weighted linear regression was used since the absolute error increased with concentration. More weight was given to the smaller (lower error) concentrations than to the larger (higher error) ones. The weighting factor used was $1/\text{s.d.}^2$ for each of the concentration levels (**1**).[6]

where:

S_T = overall precision,
S_o = single operator precision, and
X = cyanide concentration, mg/L.

18.1.6 The precision and bias for Test Method D6888 was determined in accordance with Practice D2777. Based on the results of 10 operators in 10 laboratories, the overall and single operator precision and method bias data are shown in Table 2 of Test Method D6888. The precision and bias were determined for available cyanide using a synthetic wastewater matrix.

18.2 *Bias:*

18.2.1 Recoveries of known amounts of cyanide from Reagent Water Type II and selected water matrices are shown in Table 3 and Table 4.

18.2.2 Bias was determined in alkaline reagent water (0.25 M NaOH) for ion chromatography as the determinative step during an interlaboratory study[7] in accordance with Practice D2777. The statistical summary for ion chromatography as the determinative step is shown in Table 5.

18.3 The bias for Test Method D6888 was determined for available cyanide in a synthetic wastewater in accordance with Practice D2777. This test method can also be used as a determinative step for total cyanide after distillation.

18.4 The precision and bias information given in this section may not apply to waters of untested matrices.

TEST METHOD B—CYANIDES AMENABLE TO CHLORINATION (CATC) BY THE DIFFERENCE

19. Scope

19.1 This test method covers the determination of cyanides amenable to chlorination in water.

19.2 Iron cyanides are the most commonly encountered compounds not amenable to chlorination.

19.3 This test method has been used on reagent, surface, and industrial waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

20. Interferences

20.1 All the chemical compounds listed in Section 6 can interfere. See Practice D7365 for further discussion on interferences. Alternatively, analyze the samples for available cyanide as described in Test Method D6888, which is less susceptible to interference than this method.

20.2 For the removal of these interferences, proceed as instructed in Practice D7365 and Sections 10 and 11.

20.3 This test method can be affected by compounds that are converted during chlorination to volatile compounds which are collected in the absorption solution and can interfere in the final determination.

20.4 If the calculated result is significantly negative, interferences are present. In this case, Test Method D6888 can be used to determine available cyanide.

21. Apparatus

21.1 The schematic arrangement of the distillation system is shown in Fig. 1.

21.2 For the required apparatus, refer to Section 7.

22. Reagents and Materials

22.1 Refer to Section 8.

23. Procedure

23.1 *Sample Preparation*—Divide the sample into two equal portions of 500 mL or less. Determine the total cyanide in one portion as indicated in 23.2. Place the other portion in a 1-L beaker and chlorinate as outlined in the following steps.

[6] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting RR:D19-1161.

TABLE 4 Selected Water Matrices (Test Method A)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	%Bias	Statistical Significance, 95 % CL
Colorimetric	0.060	0.060	25	0.0145	0.000	0	No
	0.500	0.489	26	0.0501	–0.011	–3	No
	0.900	0.959	24	0.0509	0.059	7	Yes
Electrode	0.060	0.058	14	0.0071	–0.002	–3	No
	0.500	0.468	21	0.0414	–0.032	–6	No
	0.900	0.922	19	0.0532	0.022	2	No
	5.00	5.13	20	0.2839	0.13	3	No
Titrimetric	2.00	2.80	18	0.8695	0.80	40	Yes
	5.00	5.29	18	1.1160	0.29	6	No
	5.00	5.75	18	0.9970	0.75	15	Yes

TABLE 5 Final Statistical Summary for Ion Chromatography as the Determinative Step

	Sample A	Sample D	Sample B	Sample E	Sample C	Sample F	A + Sulfide	D + Sulfide
Number of retained values	7	7	7	7	7	7	7	7
True Concentration (C),µ g/L	251	217	866	736	43.3	34.6	251	217
Mean Recovery (XBAR)	250	222	958	801	44	39	248	221
Percent Recovery	99.5	10.2	111	109	100	110	99.0	102
Overall Standard Deviation, (st)	17.8	20.1	58.8	41.7	7.3	4.6	18.4	13.2
Overall Relative Standard Deviation,%	7.10	9.08	6.14	5.21	16	12	7.39	5.95
Number of retained pairs	7	7	7	7	7	7	7	7
Single-Operator Standard Deviation, (so)	9.35		18.0		4.6		8.54	
Analyst Relative Deviation,%	4.01		2.12		11		3.72	
Bias	–0.46	2.11	10.61	8.83	2.6	13	–1.02	2.04

NOTE 1—Samples prepared in alkaline reagent water (0.25M NaoH). Samples A+Sulfide and D+Suflide contain 1 mg/L sulfide to test for potential interference.

NOTE 5—Protect the solution in the beaker from ultraviolet radiation by wrapping the beaker with aluminum foil or black paper and cover with a wrapped watch glass during chlorination.

23.1.1 Place the beaker on a magnetic stirrer, insert a TFE fluorocarbon-coated stirring bar in the beaker, and start stirring.

23.1.2 If necessary, adjust the pH to between 11 and 12 with NaOH solution (40 g/L).

23.1.3 Add $Ca(OCl)_2$ solution (50 g/L) 3 drops at a time until there is an excess of chlorine indicated on a strip of potassium iodide-starch test paper previously moistened with acetic acid solution.

23.1.4 Maintain the pH and excess chlorine for 1 h while stirring. Add $Ca(OCl)_2$ solution or NaOH solution, or both, 2 drops at a time when necessary.

23.1.5 At the end of the hour remove any residual chlorine by the dropwise addition of $NaAsO_2$ solution (2 g/100 mL) or by adding 8 drops of H_2O_2 solution (3 %) followed by 4 drops of $Na_2S_2O_3$ solution (500 g/L). Test with potassium iodide-starch test paper.

23.2 Follow steps 16.1.1 through 16.1.16 for Test Method A.

24. Calculation

24.1 Calculate the total cyanide in each portion of the sample following Eq 1, Eq 4, or Eq 5.

24.2 Calculate the concentration of cyanide amenable to chlorination using Eq 6:

$$\text{CN, mg/L} = G - H \tag{6}$$

where:

G = cyanide, determined in the unchlorinated portion of the sample, mg/L, and
H = cyanide determined in the chlorinated portion of the sample, mg/L.

25. Precision and Bias[5]

25.1 *Precision:*

25.1.1 *Colorimetric*—Based on the results of eight operators in seven laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	S_T	=	$0.18x + 0.005$
	S_o	=	$0.06x + 0.003$
Selected Water Matrices	S_T	=	$0.20x + 0.009$
	S_o	=	$0.05x + 0.005$

25.1.2 *Titrimetric*—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	S_T	=	$0.01x + 0.439$
	S_o	=	$0.241 - 0.03x$
Selected Water Matrices	S_T	=	$0.12x + 0.378$
	S_o	=	$0.209 - 0.01x$

25.1.3 where:

S_T = overall precision,
S_o = single operator precision, and
x = cyanide concentration, mg/L.

TABLE 6 Reagent Water (Test Method B)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
	0.008	0.009	21	0.0033	0.001	13	No
Colorimetric	0.019	0.023	20	0.0070	0.004	21	Yes
	0.080	0.103	20	0.0304	0.018	23	Yes
	0.191	0.228	21	0.0428	0.037	19	Yes
	1.00	0.73	18	0.350	−0.27	−27	Yes
Titrimetric	1.00	0.81	18	0.551	−0.19	−19	No
	4.00	3.29	18	0.477	−0.71	−18	Yes

25.2 *Bias*—Recoveries of known amounts of cyanide amenable to chlorination from reagent water Type II and selected water matrices were as shown in Table 6 and Table 7.

25.3 The precision and bias information given in this section may not apply to waters of untested matrices.

TEST METHOD C—WEAK ACID DISSOCIABLE CYANIDES

26. Scope

26.1 This test method covers the determination of cyanide compounds and weak acid dissociable complexes in water.

26.2 The thiocyanate content of a sample usually does not cause interference.

26.3 Any of the three procedures, titration, colorimetric, or selective ion electrode, can be used to determine the cyanide content of the absorption solution. The lower limits of detectability are the same as for Test Method A.

26.4 This test method has been used successfully on reagent and surface water and coke plant, refinery and sanitary waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

27. Interferences

27.1 All the chemical compounds listed in Section 6 can interfere. See Practice D7365 for further discussion on interferences. Alternatively, analyze the samples for available cyanide as described in Test Method D6888, which is less susceptible to interference than this method.

27.2 For the removal of these interferences proceed as instructed in Practice D7365 and Sections 10 and 11.

28. Apparatus

28.1 The schematic arrangement of the distillation system is shown in Fig. 1.

28.2 The required equipment, instruments, and parts are listed in Section 7.

29. Reagents and Materials

29.1 Refer to Section 8.

29.2 *Methyl Red Indicator Solution.*

30. Procedure

30.1 *Distillation Procedure:*

30.1.1 Set up the apparatus as shown in Fig. 1.

30.1.2 Add 10.0 mL of NaOH solution (40 g/L) to the absorber. Dilute with water to obtain an adequate depth of liquid. Do not use more than 225 mL of total volume in the absorber.

30.1.3 Attach the absorber to the vacuum and connect to the condenser.

30.1.4 Place 500 mL of sample in the flask. If cyanide content is suspected to be more than 10 mg/L, use an aliquot so that no more than 5 mg of cyanide are in the flask, and dilute to 500 mL with water.

30.1.5 Connect the flask to the condenser.

30.1.6 Turn on the vacuum and adjust the air flow to approximately 1 bubble per second entering the boiling flask through the air-inlet tube.

30.1.7 Add 20 mL each of the acetate buffer and zinc acetate solutions through the air-inlet tube. Add 2 or 3 drops of methyl red indicator solution.

30.1.8 Rinse the air-inlet tube with a few mL of water and allow the air flow to mix the content of the flask. (If the solution is not pink, add acetic acid (1 + 9) dropwise through the air-inlet tube until there is a permanent color change.)

30.1.9 Turn on the condenser cooling water, heat the solution to boiling, taking care to prevent the solution from backing into the air inlet tube.

30.1.10 Maintain the air flow as in 30.1.6.

30.1.11 Reflux for 1 h.

30.1.12 Turn off the heat, but maintain the air flow for at least an additional 15 min.

30.1.13 Quantitatively transfer the absorption solution into a 250-mL volumetric flask. Rinse the absorber and its connecting tubes sparingly with water and add to volumetric flask.

30.1.14 Dilute to volume with water and mix thoroughly.

30.1.15 Determine the concentration of cyanide in the absorption solution by one of the three procedures desceibed in 16.2, 16.3, or 16.4.

31. Calculation

31.1 Calculate the concentration of weak acid dissociable cyanide in the sample following Eq 1, Eq 4, or Eq 5.

32. Precision and Bias[5]

32.1 *Precision:*

32.1.1 *Colorimetric*—Based on the results of nine operators in nine laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows: