Designation: D2036 – 09 (Reapproved 2015)

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 – 18
Test Method B Cyanides Amenable to Chlorination[2] by Difference	19 – 25
Test Method C Weak Acid Dissociable Cyanides	26 – 32
Test Method D Cyanides Amenable to Chlorination without Distillation (Short-Cut Method)	33 – 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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 5.1, 8.8, 8.18, Section 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
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
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

[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.

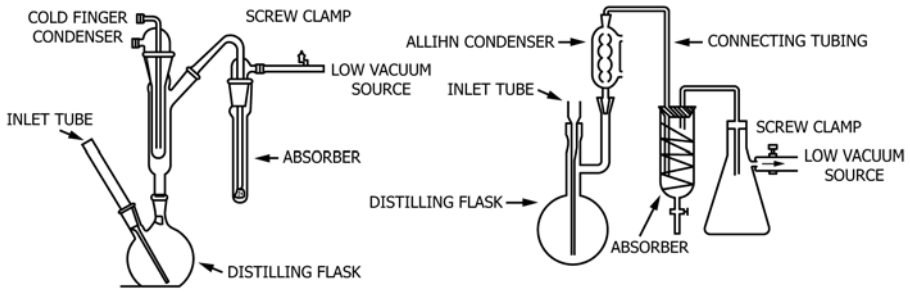

FIG. 1 Cyanide Distillation Apparatus

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions:*

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

3.2 *Acronyms:*

3.2.1 *FIA, n*—flow injection analysis

3.2.2 *HPLC, n*—high performance liquid chromatography

3.2.3 *IC, n*—ion chromatography

3.2.4 *PAD, n*—pulsed amperometric detection

4. Summary of Test Method

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 Specification 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 ($NaC_2H_3O_2·3H_2O$) 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 Section 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* ($Pb(C_2H_3O_2)_2·3H_2O$), 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 ($MgCl_2·6H_2O$) 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

[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.

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. 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.

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

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 Method D6888 (16.6). See 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:*

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	-

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 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:

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

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

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

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1131. Contact ASTM Customer Service at service@astm.org.

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

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:

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

$$S_T = 0.057x + 3.19$$

$$S_o = 0.020x + 3.90$$

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/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

[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 Research Report RR:D19-1161. Contact ASTM Customer Service at service@astm.org.

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.

portion as indicated in 23.2. Place the other portion in a 1-L beaker and chlorinate as outlined in the following steps.

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:

$$\text{CN, mg/L} = G - H \quad (6)$$

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

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
Colorimetric	0.008	0.009	21	0.0033	0.001	13	No
	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
Titrimetric	1.00	0.73	18	0.350	−0.27	−27	Yes
	1.00	0.81	18	0.551	−0.19	−19	No
	4.00	3.29	18	0.477	−0.71	−18	Yes

x = cyanide concentration, mg/L.

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 described 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:*

TABLE 7 Selected Water Matrices (Test Method B)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.008	0.013	17	0.0077	0.005	63	Yes
	0.019	0.025	18	0.0121	0.006	32	Yes
	0.080	0.100	18	0.0372	0.020	25	Yes
	0.191	0.229	18	0.0503	0.038	20	Yes
	1.00	1.20	18	0.703	0.20	20	No
Titrimetric	1.00	1.10	18	0.328	0.10	10	No
	4.00	3.83	18	0.818	−0.17	−4	No

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:

Reagent Water	S_T	=	$0.09x + 0.010$
	S_o	=	$0.08x + 0.005$
Selected Water Matrices	S_T	=	$0.08x + 0.012$
	S_o	=	$0.05x + 0.008$

32.1.2 *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	=	$0.09x + 0.004$
	S_o	=	$0.02x - 0.009$
Selected Water Matrices	S_T	=	$0.08x + 0.005$
	S_o	=	$0.02x + 0.004$

32.1.3 *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	=	$0.532 - 0.10x$
	S_o	=	$0.151 - 0.01x$
Selected Water Matrices	S_T	=	$0.604 - 0.06x$
	S_o	=	$0.092 + 0.02\ x$

32.1.4

where:

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

32.2 *Bias*—Recoveries of known amounts of cyanide from reagent water Type II and selected water matrices were as shown in Table 8 and Table 9.

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

TEST METHOD D—CYANIDES AMENABLE TO CHLORINATION WITHOUT DISTILLATION, SHORT-CUT METHOD

33. Scope

33.1 This test method covers the determination of free CN^- and CN^- complexes that are amenable to chlorination in water. The procedure does not measure cyanates nor iron cyanide complexes. It does, however, determine cyanogen chloride and thiocyanate.

33.2 Modification is outlined for its use in the presence of thiocyanate.

34. Interferences

34.1 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.

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

34.3 The thiocyanate ion which reacts with chloramine-T will give a positive error equivalent to its concentration as cyanide.

34.4 Color and turbidity can interfere.

34.4.1 When color or turbidity producing substances are present, it is recommended that Test Method B or C be used.

34.4.2 Color and turbidity can be extracted from some samples with chloroform without reduction of the pH.

34.4.3 It is possible with some samples to compensate for color and turbidity by determining the absorbance of a second sample solution to which all reagents except chloramine-T have been added.

34.5 Reducing compounds such as sulfites can interfere by preferentially reacting with chloramine-T.

34.6 The color intensity and absorption is affected by wide variations in the total dissolved solids content of the sample.

34.6.1 For samples containing high concentrations of dissolved solids, 3000 to 10 000 mg/L, add 6 g of NaCl to each litre of NaOH solution (1.6 g/L) used to prepare the standards. For samples containing dissolved solids concentration greater than 10 000 mg/L, add sufficient NaCl to the NaOH solution to approximate the dissolved solids content.

35. Apparatus

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

35.2 *Water Bath,* capable of maintaining temperature at 27 ± 1°C.

36. Reagents and Materials

36.1 Refer to Section 8.

TABLE 8 Reagent Water (Test Method C)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.030	0.030	25	0.0089	0.000	0	No
	0.100	0.117	27	0.0251	0.017	17	Yes
	0.400	0.361	27	0.0400	−0.039	−10	Yes
Electrode	0.030	0.030	21	0.0059	0.000	0	No
	0.100	0.095	21	0.0163	−0.005	−5	No
	0.400	0.365	21	0.0316	−0.035	−9	No
	1.000	0.940	21	0.0903	−0.060	−6	No
Titrimetric	1.00	1.35	18	0.4348	0.35	35	Yes
	1.00	1.38	18	0.3688	0.38	38	Yes
	4.00	3.67	18	0.1830	0.33	−8	No

TABLE 9 Selected Water Matrices (Test Method C)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.030	0.029	15	0.0062	0.001	3	No
	0.100	0.118	24	0.0312	0.018	18	Yes
	0.400	0.381	23	0.0389	−0.019	−5	Yes
Electrode	0.030	0.029	20	0.0048	−0.001	−3	No
	0.100	0.104	21	0.0125	0.004	4	No
	0.400	0.357	21	0.0372	−0.043	−11	No
	1.000	0.935	21	0.0739	−0.065	−7	No
Titrimetric	1.00	1.55	18	0.5466	0.55	55	Yes
	1.00	1.53	18	0.4625	0.53	53	Yes
	4.00	3.90	18	0.3513	−0.10	−3	No

36.2 *Pyridine-Barbituric Acid Reagent*—For the preparation of this reagent, refer to 8.15; however, for this test method, prepare a fresh solution weekly. Longer storage affects the results of the test.

36.3 *EDTA Solution* (18.5 g/L)—Dissolve 18.5 g of the disodium salt of ethylenediamine tetraacetic acid dihydrate in water and dilute to 1 L.

36.4 *Formaldehyde Solution* (10 %) —Dilute 27 mL of formaldehyde (37 %) to 100 mL.

36.5 *Hydrochloric Acid* (HCl) (sp gr 1.19) (1 + 9)—Slowly add 1 volume of concentrated HCl (sp gr 1.19) to 9 volumes of water, stirring during the addition.

36.6 *Phosphate Buffer* Solution (138 g/L)—Dissolve 159 g of sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) in water, dilute to 1 L and refrigerate.

36.7 *Sodium Carbonate* (Na_2CO_3), anhydrous.

36.8 *Sodium Chloride* (NaCl), crystals.

37. Standardization

37.1 From the cyanide standard solutions, pipet a series of aliquots containing from 0.5 to 5.0 µg of cyanide in volumes not exceeding 20 mL into 50-mL volumetric flasks.

37.2 Dilute each solution to 20 mL with NaOH solution (1.6 g/L). Follow 38.3 through 38.7 of the procedure.

37.3 Calculate the absorption factor (17.2.1).

38. Procedure

38.1 Adjust the pH of a small volume of sample (50 mL) to between 11.5 and 11.9. If the addition of acid is needed, add a small amount (0.2 to 0.4 g) of sodium carbonate and stir to dissolve. Then add dropwise while stirring HCl solution (1 + 9). For raising the pH, use NaOH solution (40 g/L).

38.2 Pipet 20.0 mL of the sample into a 50-mL volumetric flask. If the cyanide concentration is greater than 0.3 mg/L, use a smaller aliquot and dilute to 20 mL with NaOH solution (1.6 g/L). Do not exceed the concentration limit of 0.3 mg/L.

38.3 To ensure uniform color development, both in calibration and testing, it is necessary to maintain a uniform temperature. Immerse the flasks in a water bath held at 27 ± 1°C for 10 min before adding the reagent chemicals and keep the samples in the water bath until all the reagents have been added.

38.4 Add 4 mL of phosphate buffer and swirl to mix. Add one drop of EDTA solution, and mix.

38.5 Add 2 mL of chloramine-T solution and swirl to mix. Place 1 drop of sample on potassium iodide-starch test paper which has been previously moistened with acetate buffer solution. Repeat the chloramine-T addition if required. After exactly 3 min, add 5 mL of pyridine-barbituric acid reagent and swirl to mix.

38.6 Remove the samples from the water bath, dilute to volume and mix. Allow 8 min from the addition of the pyridine-barbituric acid reagent for color development.

38.7 Determine the absorbance at 578 nm in a 1.0-cm cell versus water.

38.8 Calculate the concentration of cyanide as milligrams per litre, in the original sample following equations given in 17.2.

TABLE 10 Reagent Water (Test Method D)

Amount Added, mg/L		Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
CN	SCN						
0.005		0.007	42	0.0049	0.002	40	Yes
0.027		0.036	41	0.0109	0.009	25	Yes
0.090		0.100	42	0.0167	0.010	11	Yes
0.090	0.080	0.080	39	0.0121	–0.010	11	Yes
0.270		0.276	42	0.0320	0.006	2	No

38.9 If the presence of thiocyanate is suspected, pipet a second 20-mL aliquot of pH-adjusted sample solution into a 50-mL volumetric flask. Add 3 drops of 10 % formaldehyde solution. Mix and allow to stand 10 min. Place in a water bath at 27 ± 1°C for an additional 10 min before the addition of the reagent chemicals and hold in the bath until all reagents have been added.

38.10 Continue with 38.4 through 38.7.

38.11 Calculate the concentration of cyanide, in milligrams per litre, in the original sample following equations given in 17.2.

38.12 In the presence of thiocyanate, cyanide amenable to chlorination is equal to the difference between the concentration of cyanide obtained in 38.8 and that obtained in 38.11.

39. Precision and Bias[8]

39.1 *Precision:*

39.1.1 Based on the results of 14 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 =	$0.10x + 0.006$
	S_o =	$0.07x + 0.005$
Selected Water Matrices	S_T =	$0.11x + 0.007$
	S_o =	$0.02x + 0.005$

39.1.2

where:

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

39.2 *Bias*—Recoveries of known amounts of cyanide from reagent water Type II, seven creek waters, one diluted sewage (1 + 20) and one industrial waste water are as shown in Table 10 and Table 11.

39.3 This precision and bias information may not apply to waters of untested matrices.

40. Quality Assurance/Quality Control

40.1 *Verification of Systems for Quantifying Cyanide in the Distillate:*

40.1.1 *Titration Procedure:*

40.1.1.1 Standardize the silver nitrate solution with Potassium Chloride, NIST, at least every six months.

40.1.1.2 Titrate 100-mL aliquots of Cyanide I Solution Standard and 100-mL aliquots of Sodium Hydroxide Solution (1.6 g/L) each time the procedure is used. Duplicate titrations should check within 0.05 mL.

40.1.2 *Colorimetric Procedure:*

40.1.2.1 Prepare a series of cyanide standards, including zero (blank), based on the expected concentration range of the samples, and follow the standardization each time new reagents are prepared or every six months.

40.1.2.2 The slope (*m*) of the standard curve should check the theoretical value:

1.0-cm cell, 0.22–0.24 mg CN/L/a; 5.0-cm cell, 0.044–0.048 mg CN/L/a; 10.0-cm cell, 0.022–0.024 mg CN/L/a

40.1.2.3 At least one standard solution and one blank should be checked each time the procedure is used.

40.1.3 *Selective Ion Electrode Procedure:*

40.1.3.1 Follow the standardization procedure each time new standard solutions are prepared.

40.1.3.2 The slope of the curve should check within 90 % of the theoretical value: 59.2 mV/decade.

40.1.3.3 At least two standard solutions and one blank should be checked each time the procedure is used.

40.1.4 *Ion Chromatographic Procedure:*

40.1.4.1 At least three standard solutions and one blank should be checked each time the procedure is used.

40.1.4.2 Calibrate the ion chromatograph each time the procedure is used or whenever the eluent is changed. If the response or retention time for cyanide varies from the expected value by more than ±10 % a new calibration curve must be prepared.

40.1.4.3 One midrange standard solution and a blank should be checked each time the procedure is used or at least every 20 samples. If the response or retention time varies from the expected value by more than ±10 % repeat the test using fresh standards.

40.2 *Verification of the Distillation Procedure:*

40.2.1 Verify the distillation procedure as described in sections 40.3 to 40.8.

NOTE 6—With careful selection of concentration all four quantification procedures can be performed on the same distillate solution. (See Guide D5788.)

40.3 *Initial Demonstration of Laboratory Capability:*

40.3.1 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1074. Contact ASTM Customer Service at service@astm.org.

TABLE 11 Selected Water Matrices (Test Method D)

Amount Added, mg/L		Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
CN	SCN						
0.005		0.003	40	0.0042	–0.002	40	Yes
0.027		0.026	42	0.0093	–0.001	4	No
0.090		0.087	42	0.0202	–0.003	3	No
0.090	0.080	0.068	37	0.0146	–0.022	24	Yes
0.270		0.245	41	0.0319	–0.025	9	Yes

40.3.2 Analyze seven replicates of a standard solution prepared from an IRM containing a known concentration of cyanide in reagent water. Each replicate should be taken through the entire analytical test (that is, the distillation and determinative step) including preservation and any pretreatment used to remove interferences. The replicates may be intersected with samples.

40.3.3 Calculate the mean and standard deviation of the seven values and refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

40.4 *Laboratory Control Sample (LCS):*

40.4.1 To ensure that the test method is in control, analyze an LCS containing cyanide at the appropriate concentration range for each analytical batch of 10 samples. For batches of less than 10 samples analyze at least one LCS. The LCS should be taken through the entire analytical procedure. The LCS is considered in control if the recovery is 85-115 %. If the LCS falls outside these limits halt the analysis of samples until the problem is corrected, upon which the samples should be reanalyzed if possible. If samples cannot be reanalyzed, qualify the data that the LCS was not within the performance criteria of the test method.

40.5 *Method Blank:*

40.5.1 Analyze a reagent water test blank with each analytical batch of 10 samples or at least once daily if less than 10 samples are analyzed in a given day. The concentration of cyanide should be less than the reporting limit for the corresponding method or else sample analyses are halted until the problem is corrected. Affected samples should be reanalyzed or qualified.

40.6 *Matrix Spike (MS):*

40.6.1 To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each analytical batch by fortifying a known concentration of cyanide and taking it through the entire analytical procedure.

40.6.2 The matrix spike must produce a concentration that is 2 to 5 times the background concentration or 10 to 50 times the detection limit of the test method, whichever is greater. Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\,\frac{|\,A(V_s + V) - BV_s\,|}{CV}$$

where:

A = concentration found in spiked sample,
B = concentration found in unspiked sample,
C = concentration of analyte in spiking solution,
V_s = volume of sample use, and
V = volume of spiking solution added.

40.6.3 The percent recovery of the spike shall fall within 70–130 % or else one of the following must be employed: the matrix interference should be removed, all samples in the batch must be reanalyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that the matrix spike does not fall within the performance criteria of the test method.

40.7 *Duplicate:*

40.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each analytical batch. If the concentration of cyanide is less than five times the detection limit for the method, a matrix spike duplicate (MSD) should be used. Calculate the standard deviation of the duplicate values and compare to the single operator precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information applying the F test.

40.7.2 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

40.8 *Independent Reference Material (IRM):*

40.8.1 In order to verify the quantitative value obtained in the method, analyze an IRM, preferably analyzed as a regular sample at least once a quarter. The observed concentration should fall within the limits set by the outside source of the IRM.

41. Keywords

41.1 colorimetric; cyanides amendable to chlorination; distillation; ion chromatography; ion electrode; titration; total cyanide; weak acid dissociable cyanides

ANNEX

(Mandatory Information)

A1. SPOT TEST FOR SAMPLE SCREENING

A1.1 Scope

A1.1.1 The spot test procedure allows a quick screening of the sample to establish if more than 0.05 mg/L (ppm) of cyanides amenable to chlorination, cyanogen chloride, or thiocyanate are present in water, waste water, and saline water.

A1.1.2 The test may also be used to establish the presence and absence of cyanogen chloride by omitting the addition of chloramine-T.

A1.1.3 With the addition of formaldehyde to the sample, the amenable cyanide can be masked and under these conditions, the test is specific to thiocyanate. It is possible therefore to distinguish between the presence of cyanide and thiocyanate or possibly judge the relative levels of concentration for each.

A1.1.4 With practice or dilution, the test can be used to estimate the approximate concentration range of these compounds, judging from the color development and comparing it to similarly treated samples of known concentration.

A1.2 Interferences

A1.2.1 All the chemical compounds listed in Section 6, with the exception of the nitrites, may interfere. For their removal, refer to Sections 10 and 11.

A1.2.2 The thiocyanate ion reacts in the same manner as the cyanide. The cyanide can be masked and then the test is specific for thiocyanate.

A1.2.3 The presence of large amounts of reducing substances in the sample interferes by consuming the chloramine-T added. Repeat the chloramine-T addition, if necessary.

A1.3 Apparatus

A1.3.1 *Spot Plate,* porcelain with 6 to 12 cavities preferred.

A1.4 Reagents and Materials

A1.4.1 Refer to Sections 8 and 36.

A1.4.2 *Formaldehyde,* 37 %, pharmaceutical grade.

A1.4.3 *Hydrochloric Acid* (1 + 9)—Mix 1 volume of concentrated (HCl (sp gr 1.19) with 9 volumes of water.

A1.4.4 *Sodium Carbonate,* anhydrous Na_2CO_3.

A1.5 Procedure

A1.5.1 If the solution subject to spot tests is alkaline in a pH range greater than 10, neutralize a 20 to 25-mL portion.

A1.5.1.1 Add 1 drop of phenolphthalein indicator solution. If the sample remains colorless, proceed to A1.5.2.

A1.5.1.2 If the sample turns red, add approximately 250 mg of sodium carbonate and mix to dissolve.

A1.5.1.3 Add HCl (1 + 9) dropwise while mixing until colorless.

A1.5.2 Place 3 drops of sample and 3 drops of reagent water (for a blank) on a white spot plate.

A1.5.3 To each cavity, add 1 drop of chloramine-T solution and mix with a clean stirring rod.

A1.5.4 To each cavity add 1 drop of phosphate buffer.

A1.5.5 Add 1 drop of pyridine-barbituric acid solution to each and again mix with a stirring rod.

A1.5.6 After 1 min, the sample spot will turn pink to red if 0.05 mg/L or more of CN is present. The blank spot will be faint yellow due to the color of the reagents. Until familiarity with the spot test is gained, it may be advisable to use, instead of the reagent water blank, a standard solution containing 0.05 mg/L CN for color comparisons. This standard can be made up by diluting the KCN standard solution (8.8.3).

A1.5.7 If the presence of thiocyanate is suspected, test a second sample pretreated as follows: Heat a 20 to 25-mL sample in a water bath at 50°C; add 0.1 mL of formaldehyde and hold for 10 min. This treatment will mask up to 5 mg CN/L.

A1.5.8 Repeat the spot test with the treated sample. Color development indicates the presence of thiocyanate. Comparing the intensity of the colors in the two spot tests is useful in judging whether both compounds are present and, if so, the relative concentration of cyanide and thiocyanate.

APPENDIX

(Nonmandatory Information)

X1. CYANIDE

X1.1 Introductory Comments

X1.1.1 Cyanides are used extensively in metal finishing processes and heat treatment of steel, and are a significant constituent of wastes from coke oven and blast furnace operations. As a toxic contaminant of effluents, they usually appear in the waste waters from quenching, gas scrub waters, and rinse water effluent from electroplating plants. The toxic effects of cyanide are so severe and established toxicity levels so low (<0.1 mg/L) that regulatory concern and waste treatment efforts by industry need dependable analytical procedures and a better understanding of the various cyanide complexes that may be encountered.

X1.2 Molecular Hydrogen Cyanide, Cyanides Amenable to Chlorination, Iron Cyanides

X1.2.1 Toxicological investigations by Doudoroff and others have indicated that the acute toxicity of polluted water is caused by the molecular hydrogen cyanide (undissociated HCN) as opposed to the cyanide ion (CN^-) that may be equally present (**2-4**). Actually, Milne suggested complexing the molecular HCN with metal salts as a waste treatment process (**5**).

X1.2.2 A number of analytical methods were proposed to allow a quantitative distinction for the molecular HCN to establish the acute toxicity levels of surface waters when cyanide toxicity is suspected (**6-10**). The first question we have to raise when evaluating these various analytical procedures is whether the premise regarding the distinction between molecular or undissociated HCN hydrogen cyanide on the one hand and cyanide ions on the other hand is valid or not. The distinction desired is actually the dissociated CN^- as distinct from the CN^- tightly bound in the metal complex. Another term referred to by the authors in reference is "free cyanide." This term doesn't have any toxicological significance and is commonly used in the electroplating industry and refers to the cyanide ion that can be titrated with silver nitrate (Liebig Titration), forming an insoluble silver cyanide precipitate when the free cyanide available for complexing the silver is exhausted.

X1.2.3 Lancy and Zabban have shown (**11**) that in solutions containing the various metal cyanide complexes, the difference in cyanide ion activity is due to the difference in measurable dissociation constants for each of the metal cyanide complexes investigated.

X1.2.4 Critical evaluation of the toxicity investigations with various metal cyanide complexes reveals that these reports confirm the great differences in dissociation by the various metal cyanide complexes.

X1.2.5 Both Milne (**12**) and Doudoroff (**13**) show that in the critical concentration of 0.01 to 0.5 mg/L of CN at a pH of 7.5, HCN formation is favored and will be maintained if depleted by further dissociation of the cyanide complex. Lowering the pH (that is, increasing the hydrogen ion concentration by 0.3 pH units) doubles the HCN content.

X1.2.6 Doudoroff has found that the toxicity of zinc-, cadmium-, and copper-cyanide compounds is probably greater than equal concentrations of sodium cyanide. The synergistic toxic effects, when both zinc and copper ions are combined with cyanide, are known. Additional evidence regarding the toxicity of copper, silver, and nickel cyanide complexes in low concentrations was reported (**3, 13, 14**). Doudoroff, on the other hand, shows that the iron cyanides do not dissociate to any measurable extent and therefore are not toxic to fish (**2, 3, 15**).

X1.2.7 Differentiation between toxic and nontoxic cyanide was designated "cyanides amenable to chlorination" by Lancy and Zabban (**16**). Differentiation is based on the oxidizing effect of chlorine. Resistance of the iron cyanide compounds to oxidation is due to lack of dissociation rendering them nontoxic to fish. Test for "Cyanides Amenable to Chlorination Without Distillation" is based on rapid dissociation of cyanide and complexing with chloramine-T. First, the sample aliquot is prepared in the very low concentration ranges, aiding dissociation which is accelerated by complexing the cyanide ion with chloramine-T. The latter frees additional cyanide ion to reestablish the equilibrium that was disturbed. The pH is reduced significantly by adding the pyridine-barbituric acid reagent (pH 5 to 5.5), and the sample is previously heated to accelerate the dissociation and complexing with chloramine-T. The test therefore has the necessary ability to measure certain undissociated cyanides, which could be converted by dissociation to toxic cyanides as a result of pH changes or dilution of the sample.

X1.2.8 All metal cyanide complexes are in equilibrium with the hydrolyzed HCN molecule, the concentration being dependent on the pH of the water and the dissociation constant of the particular metal cyanide complex present. The tightest complex is formed with iron. Since there is little dissociation, we may say that the ferrocyanide and ferricyanide compounds are themselves nontoxic (**17, 18**). The iron cyanide complex is so tight that the standard alkaline chlorination procedure will not affect it. Reported analytical data showing a slight reduction in ferrocyanide content, either in the chlorination step or recovery in the colorimetric analysis procedure, is most likely due to impurity in the reagent or the handling of the sample. Analytical-grade ferrocyanide when dissolved always contains some dissociated CN^-(HCN). The sample has to be handled carefully to avoid any photodecomposition which will appear as an oxidizable portion of the total ferrocyanide present (**19-21**). All other metal cyanide compounds will be chlorinated at a slower rate due to the slow dissociation of the metal cyanide complex. The equilibrium of the metal cyanide complex and molecular HCN is continuously upset, and as the dissociation occurs, the hypochlorite ion will react with the

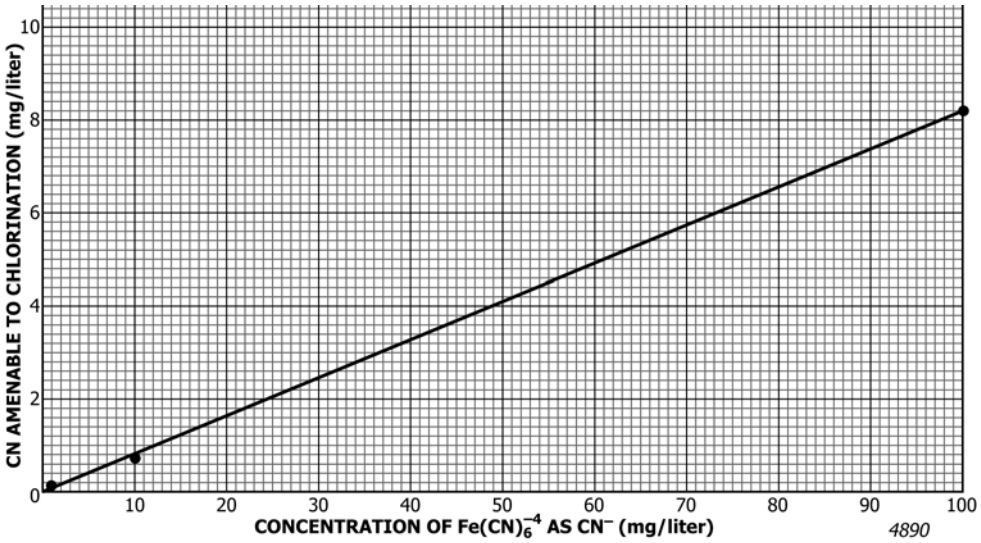

FIG. X1.1 Photodecomposition Rates for $Fe(CN)_6^{4}$ in Direct Sunlight, 20°C, pH 7, in Buffered Distilled Water, 75 mm Solution Layer, 1 h Exposure

cyanide ion, leading to further dissociation of the metal cyanide complex and then allowing further oxidation by chlorination. This implies a time dependence regarding the chlorination reaction with the cyanide ion that is complexed by such metals as silver, gold, and nickel. The chlorination of nickel cyanide at a concentration of 20 mg/L CN, as an example, may not be complete after 1 h even when hypochlorite was added at a 10 % excess of the stoichiometric amount (**16, 22, 23**). Because iron cyanide complexes are not destroyed by the practical methods of "alkaline chlorination" and cyanide in contact with iron salts causes iron cyanide to be always present in metal finishing waste, the question of proper waste treatment, or its lack, was many times raised when analyzing industrial waste using the standard analytical procedures. There is important practical value, therefore, that a distinction be made and analytical procedures be developed for "Cyanides Amenable to Chlorination" (**11, 16**). As it has been established that the ferrocyanide complex is not toxic (**2, 3, 17, 18**) it might be assumed that a low-cyanide concentration of 1 to 10 mg/L; if not amenable to chlorination such as iron cyanides, would have no toxic effect on the environment. However, this assumption is based on the following two factors:

X1.3 The Iron Cyanides Undergo Dissociation from Photodecomposition (18 and 21)

X1.3.1 Under strong sunlight, 10 mg/L iron cyanide, expressed as CN^-, may release 1 mg/L HCN in 1 h (Fig. X1.1).

X1.4 Dilution and Dispersion of the Treated Waste in the Receiving Waters

X1.4.1 The kind of dilution, mixing in the diluting stream, clarity of the receiving waters, and the quantity of HCN release that may be expected are dependent upon particular environmental conditions, considering that only the top layers of the receiving waters will be subject to the strong sunlight to cause decomposition. Oxidation by air and bacterial decomposition in the receiving waters will be additional factors mitigating against the development of toxic concentration levels.

X1.4.2 Deliberate complexing of simple cyanides with iron salts as an economical means of waste treatment naturally should be unacceptable. Higher concentrations of iron cyanides, in view of the foregoing, require treatment. Suitable processes for the oxidative destruction of iron cyanides are available (**24**), leading to the complete destruction of the cyanide and precipitation of iron oxide. Insoluble iron cyanide precipitates are soluble in alkali. Therefore, their being insoluble under normal conditions is not an ensurance that the environment is protected.

X1.5 Cyanogen Chloride

X1.5.1 Presently the destruction of cyanide compounds in waste treatment processes is done by oxidation with hypochlorite (OCl^-) because the oxidation reaction is rapid and can be carried to completion using near stoichiometric equivalent of the reacting chemical. The chlorination reaction has to be conducted at an alkaline pH because the first reaction product formed is cyanogen chloride, a toxic gas, having very low solubility. The toxicity of cyanogen chloride may exceed the toxicity of HCN, both in water and in the atmosphere (<0.1 mg/L) (**25, 26**). Cyanogen chloride hydrolyzes at an alkaline pH to cyanate (CNO^-). The rate of hydrolysis is dependent on the pH conditions and the available excess chlorine, the higher the pH or the more chlorine present, the faster will the reaction go to completion. At a pH of 9, with no excess chlorine present, cyanogen chloride may persist in the treated water for more than 24 h (**27-29**). In view of the low solubility of cyanogen chloride and the time dependence for its hydrolysis, it is desirable to maintain the alkalinity during chlorination at pH 11 or higher. A pH of 12 to 13 may be required when the chlorination reaction is carried out on a waste water containing high concentrations of cyanide (>100 mg/L). The low solubility of cyanogen chloride is reduced further by the reaction heat

generated upon addition of chlorine. The vapor pressure of the cyanogen chloride gas is increased. Rapid hydrolysis of the cyanogen chloride is the only means available to avoid the escape of cyanogen chloride into the atmosphere. When conducting continuous treatment of an effluent, the pH of the waste stream is lowered after a few minutes of reaction time because a neutral effluent has to be discharged. After the pH is reduced, any cyanogen chloride that has not yet undergone hydrolysis will escape as the toxic cyanogen chloride in the effluent. At pH 11 and at 10°C, the half-life period of cyanogen chloride before hydrolysis to CNO^-, and in the absence of excess chlorine, is 12.5 min (**27-29**). It is regrettable that the importance of this reaction and these conditions are not appreciated by Regulatory Agencies and waste treatment engineers. Analysis for cyanogen chloride is not performed, whereas concern is shown for the possible cyanate content of a treated waste. An analytical procedure for the distinction between HCN, ferro- and ferricyanide, respectively was published by Kruse and Thibault (**10**).

X1.6 Cyanate Compounds

X1.6.1 As discussed in Section X1.5, the cyanogen chloride that is formed due to the reaction of OCl^- with cyanide ions and HCN during the chlorination reaction will hydrolyze to cyanate (CNO^-). The reported toxicity of cyanate in water is >100 mg/L. The reversion of cyanate to cyanide was attempted with photodecomposition and reduction, but could not be accomplished (**30**). Theoretical calculations also indicate that cyanate cannot be reduced to cyanide.

X1.6.2 Acidification and dilution of the cyanate leads to hydrolysis of cyanate to the ammonium ion (NH_4^+). Ammonia toxicity was reported in the 2 to 2.5 mg/L range in hard water (**17**). Doudoroff reports toxic effects at even lower levels (<1 mg/L), (**25**). It can be assumed therefore that the toxicity of cyanate is mainly due to the fact that it will yield ammonia. Since chlorination is conducted at high pH, and the treated waste normally then neutralized, further pH reduction may occur due to the lower pH condition of natural waters. Therefore, we may assume that harmful concentrations of cyanate will not be easily encountered in a natural environment. A cyanate determination within ASTM has not yet been formalized. Recommended analytical procedures are available from the literature (**30-33**).

X1.7 Thiocyanate Compounds

X1.7.1 The relatively nontoxic thiocyanate compounds (**17**) may become extremely toxic due to conversion to cyanogen chloride (see X1.5.1) when a waste stream containing the thiocyanate ion undergoes chlorination for disinfection (**25, 26**). The probable reaction is: $KCNS + 4Cl_2 + 4H_2O \rightarrow CNCl + KCl + H_2SO_4 + 6\ HCl$.

X1.7.2 According to Doudoroff, this reaction will occur even if the chlorine added to the waste stream is not sufficient to provide a residual (**25**). Thiosulfate, a common reducing chemical used to detoxify chloramines, is not as effective for cyanogen chloride unless a large excess is used (**26**).

X1.7.3 The determination for "cyanides amenable to chlorination" will also include the thiocyanate ion due to the conversion to cyanogen chloride by chloramine-T. A specific test for thiocyanates is contemplated.

X1.8 Total Cyanide

X1.8.1 Cobalt cyanide is not recovered completely during the distillation. The explanation for this condition was given by Leschber (**34**) and referred to by original investigations by Bassett and Corbet (**35**). Potassium cobalt cyanide, when boiled with dilute sulfuric acid, partially breaks down to carbon monoxide, carbon dioxide, and ammonium sulfate.

X1.8.2 The determination of total cyanide retains its significance. As discussed earlier in Section X1.2, iron cyanides will not be revealed by the Cyanides Amenable to Chlorination analysis methods. To a lesser extent, some of the nickel cyanide, cobalt cyanide, silver and gold cyanide will also not be completely recovered. Neither will the standard alkaline chlorination practices break down these complexes. It has been noted that the toxic effects of these compounds are also considerably less and of a different nature: photodecomposition for iron cyanides; slow dissociation for nickel-, cobalt-, silver-, and gold cyanides. At the same time, there are many waste treatment installations that are either not designed properly, or not operated properly; therefore, more cyanide compounds that could have been treated are discharged in the effluent. There are also some processes generating excessively large quantities of these complex cyanides, thereby producing a significant pollution hazard.

As examples, we should list:

(a) Heat treating processes;

(b) Coke and blast furnace operations;

(c) Cyanide-type processes used for stripping nickel and cobalt-nickel alloy deposits;

(d) Rinse waters from silver and gold plating operations;

(e) Accidentally mixed waste coming from nickel plating solutions and cyanide floor spill;

(f) Regeneration and backwash waters from ion exchange type waste treatment processes used for the removal of plating salts from rinse water waste. The treatment of these wastes consists usually of mixing, partially deliberately, partially due to the process, and partially accidentally, nickel and iron salts with cyanide compounds; and

(g) Some waste treatment processes still recommended the use of iron sulfate for the neutralization of cyanide salts, etc.

X1.8.3 The total cyanide determination therefore must be used to ensure good waste treatment practices. The mistaken belief that the enumerated cyanide compounds are not "toxic" must be avoided. The fact is that the toxicity is only of a lesser magnitude.

X1.9 Cyanide in Solid Waste

X1.9.1 The waste treatment needs for soluble cyanide sludges is assumed, for example, sludges from plating solutions; cyanide salts removed from heat treat pots or in frozen condition as drag-out from heat treatment; or cyanide salts as residue from the evaporation of processing solutions or rinse waters. The treatment requirements for these highly toxic residues is obvious.

TABLE X1.1 Solubility of Metal Cyanide Precipitates in Water

Precipitate	Solubility in Water, g/L	Temperature, °C
Silver cyanide	0.000028	18
Zinc cyanide	0.0058	18
Copper cyanide	0.014	20
Nickel cyanide	0.0592	18
Cadmium cyanide	17	15
Mercuric cyanide	93	14

X1.9.2 Most of the metal cyanide complexes are insoluble and are made soluble in water only in the presence of excess alkali metal cyanides. Milne (**5**) quotes a few examples which, while not complete, should be sufficient to show the insolubility of some metallic cyanides.

X1.9.3 During waste treatment, if the process is not conducted carefully, as the breakdown of the alkali metal cyanide is progressing, the metal cyanide will become insoluble, and will precipitate as the slightly soluble cyanide compound of the particular metal originally present. As seen from Table X1.1, some sludges may contain high levels of relatively insoluble metallic cyanides having high potential toxicity. Lancy and Zabban have reported (**16**) the cyanide content in the precipitates when conducting slow chlorination and with no or minimal chlorine excesses. The complete treatment and removal of the cyanide concentration in the sludge can be accomplished only by either significant chlorine excess in the waste water, or by rapid chlorination to allow breakdown of the metal cyanide complex before it is precipitated and buried in the sludge. Some newer waste treatment processes, such as treatment with peroxygen compounds, will yield considerably higher available cyanide concentrations in the sludge.

X1.9.4 Iron cyanide is always present in electroplating solutions. The concentration is usually in the range from 20 to 25 g/L. Only a small quantity of this iron cyanide will appear in the rinse water effluent, and as it escapes chlorination, it may form insoluble iron cyanide compounds with other metals present, such as copper, zinc, iron, etc. The metal iron cyanide compounds may be considered insoluble and nontoxic, but can become soluble in the alkaline range (pH > 9) if the solid waste is leached with alkaline waste. The resolubilized iron cyanide can undergo photodecomposition as discussed in Section X1.2. The insoluble iron cyanide content of solid waste may be a result of the best treatment that modern technology can do with regard to treatment and disposal of particular cyanide compounds. The usual disposal is burial or landfill where acid conditions are far more common than excessive alkalinity which would cause the redissolution.

X1.9.5 The insoluble cyanide content of a solid waste can be determined by placing a 500-mg sample with 500 mL of distilled water into the distillation flask and following the total cyanide distillation. The calculations should consider a multiplication by 1000 to give the cyanide content of the solid waste sample in ppm. Insoluble iron cyanides in the solid waste can be leached out before analysis by stirring a weighed sample for 12 to 16 h in a 10 % caustic soda solution. The leachate and wash waters of the solid waste will give the iron cyanide content of the sample using the distillation procedure. A previous chlorination will have eliminated all cyanide amenable to chlorination from the sample. The sample should not be exposed to sunlight. A method allowing differentiation between HCN, ferro- and ferricyanide, as mentioned earlier, is referenced (**10, 21**).

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