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An American National Standard

Standard Test Methods for Cyanides in Water[1]

This standard is issued under the fixed designation D 2036; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 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.

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.

1.5 Only a few organo-cyanide complexes 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 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.

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 Note 3, Note 4, Note 6, and Note 7, 5.1, and Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]

D 3370 Practices for Sampling Water from Closed Conduits[3]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]

D 5788 Guide for Spiking Organics into Aqueous Samples[3]

D 5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[5]

3. Terminology

3.1 Definitions—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Abbreviations: Abbreviations:*

3.2.1 *HPLC*—High Performance Liquid Chromatography

3.2.2 *IC*—Ion Chromatography

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

[1] These test methods are under the jurisdiction of ASTM Committee D-19 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] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] *Annual Book of ASTM Standards*, Vol 03.06.

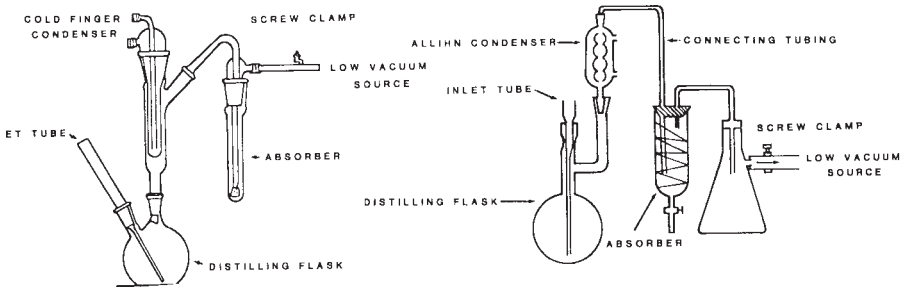

FIG. 1 Cyanide Distillation Apparatus

distillation distinguish the type of cyanide. The sodium cyanide in the absorbing solution can be determined colorimetrically, by titration or by selective ion electrode.

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 The minimum concentration of cyanide in the absorption solution that can be accurately determined colorimetrically is 0.005 mg/L, by titration 0.4 mg/L and by selective ion electrode 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.

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.

6.3 When the procedures must be revised to meet specific requirements, recovery data must be obtained by the addition of known amounts of cyanide to the sample.

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.

7.2 *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 E 60. Spectrophotometers shall conform to Practice E 275.

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 solution injection device and pulsed-electrochemical 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.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II grade of Specification D 1193.

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) (**Warning—** see Note 3) 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).

NOTE 3—**Warning**—Because KCN is highly toxic, avoid contact or inhalation (see Section 9).

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.

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. Store in a dark container.

8.18 *Sodium Arsenite Solution* (20 g/L)—Dissolve 2 g of $NaAsO_2$ in 100 mL of water.

NOTE 4—**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 Solution* (100 mM sodium hydroxide, 500 mM sodium acetate, and 0.5 % (v/v) ethylenediamine)—Dissolve 136.1 g of sodium acetate in 800-mL water. Transfer to a 2000-mL volumetric flask, add 10 mL of ethylenediamine, and dilute to mark. Sparge the solution with helium for 20 min. Add 10.4 mL of 50 % sodium hydroxide solution and allow the sparging to continue for and additional 5 min to mix.

8.26 *Ethylene diamine.*

8.27 *Helium.*

8.28 *Sodium Hydroxide Solution* (50 % W/W). Dissolve 100 g NaOH in 100 g of water or purchase a 50 % solution.

8.29 *Sodium Acetate.*

9. Hazards

9.1 **Caution**—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.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *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.

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.

10. Sample and Sample Preservation

10.1 Collect the sample in accordance with Practices D 3370.

10.2 Minimize exposure of samples to ultraviolet radiation that causes photodecomposition of some metal cyanide complexes and may significantly increase the concentration of free cyanide in the sample. It is recommended that all manipulations of the sample be performed in a well-ventilated hood under incandescent light.

10.3 Oxidizing agents (chlorine) will destroy the cyanide in storage. Sulfide can convert the cyanide to thiocyanate, especially at the pH of the stabilized sample. The presence of either oxidizing agents or sulfides should be determined before the addition of sodium hydroxide preservation or further analysis.

10.3.1 *Oxidizing Agents*—Test for the presence of chlorine by placing a drop of the sample on a strip of potassium iodide-starch test paper which has been previously moistened with the acetic acid solution. Darkening (bluish) of the test paper normally indicates the presence of chlorine. (Manganese dioxide, nitrosyl chloride, etc., if present, may also cause discoloration of the test paper.) Add sodium arsenite solution dropwise to the sample and retest. In the event that a bluish discoloration is still perceptible, repeat the sodium arsenite addition.

10.3.2 *Sulfide*—Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper which has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide. The presence of sulfide can be assumed to indicate the absence of oxidizing agents in the sample. Sulfide is removed by treating the sample with small increments of powdered lead carbonate or with the dropwise addition of lead nitrate or lead acetate solution. Black lead sulfide precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with lead acetate test paper. Immediately filter through dry paper into a dry beaker and stabilize the sample according to 10.4 or 10.5.

10.4 If the sample cannot be analyzed immediately, stabilize it by the addition of sodium hydroxide (NaOH) pellets to a pH of 12 to 12.5 and store it in a closed bottle (dark bottle if available) in a dark and cool environment.

NOTE 5—It has been determined that the use of hydrated lime, $Ca(CO)_3$, for the stabilization of effluents high in carbonate content lowers the recovery of total cyanide from samples. The task group responsible for this standard is pursuing further revision to this section.

11. Elimination of Interferences

11.1 The following treatments are for the removal or reduction of substances that can interfere in the various methods. Care must be taken to keep time of pretreatment at a minimum to avoid loss of cyanide (see 9.1).

11.2 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, (**Caution**—see Note 6). 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.

NOTE 6—**Caution:** Perform this operation in the hood and leave the sample there until it is made alkaline after the extraction.

11.3 Aldehydes combine with cyanides to form cyanohydrins which can hydrolyze to acids under distillation conditions. Hydrogen cyanide is not liberated and is not available for quantitative determination in the absorption solution. The formation of cyanohydrins also interferes in the direct colorimetric determination (Test Method D and spot test). Identification and removal of aldehydes is described in Appendix X2 .

11.3.1 Glucose and other sugars if present in the sample can also form cyanohydrins with cyanide at the pH of preservation.

11.4 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. Calcium hydroxide is added slowly with stirring to a pH of 12 to 12.5. After the precipitate settles, the supernatant liquid is decanted and used for the determination of cyanide.

11.4.1 However, if the sample contains insoluble complex cyanide compounds, they will not be included in the determination. In this event, a measured amount of well-mixed treated sample can be filtered quantitatively through a glass-fiber or a membrane filter (47-mm or less). The filter is rinsed with dilute (1 + 9) acetic acid until the effervescence ceases, and the entire filter with the insoluble material is added to the filtrate prior to distillation.

11.5 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 eliminate this interference.

11.6 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 eliminate 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.

11.6.1 Cyanide can be measured in the presence of sulfur containing compounds by using IC to separate the interferences from the cyanide (16.5).

11.7 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.

11.8 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 Either the titration, colorimetric or selective ion electrode procedure can be used to quantify the cyanide concentration.

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.

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 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.

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).

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

16.1.8 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.

NOTE 7—**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 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 four procedures (16.2, 16.3, 16.4, or 16.5).

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 Dilute to 40 mL with the NaOH solution (1.6 g/L).

16.3.2.3 Place 40 mL of NaOH solution (1.6 g/L) 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 8—Check a small portion of the solution for sulfide. If it is present, add either the $PbCO_3$ or $Pb(C_2H_3O_2)_2$ 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 9—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) (*a*) *Flow Rate*: 1.0 mL/min.

(b) (*b*) *Pulsed-Electrochemical Detector* 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.

(c) (*c*) *Column,* Dionex IonPac As 10 anion-exchange, 4 × 250 mm and matching guard column or equivalent.

(d) (*d*) *Temperature*: Ambient.

(e) (*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.

16.5.2.4 Cyanide will elute in the retention time frame of 7.5-9.0 min depending upon column effective equivalency, eluant preparation, and temperature effects. Sulfide will elute in the 4.0-6.0 min time frame and will pose no interference with the cyanide analysis.

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

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

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:

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

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

TABLE 2 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

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:

$$\text{CN, mg/L} = (ma_1 + b)\, X\, \frac{59}{X}\, X\, \frac{250}{Y} \quad (4)$$

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 [7]

18.1 *Precision*:

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*—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:

$$\text{xbar} = 1.04x + 0.35$$
$$S_T = 0.057x + 3.19$$
$$S_o = 0.020x + 3.90$$

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**).[8]

18.1.5 where:

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

18.1.6 Since this is an existing test method which has results from a minimum of three laboratories for a total of six operators, it does not require further collaborative testing in accordance with Practice D 2777.

18.2 *Bias*—Recoveries of known amounts of cyanide from Reagent Water Type II and selected water matrices are shown in Table 2 and Table 3. Data from Table 4 will be added to Table 2 on Reagent Water (Test Method A.)

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

[7] Supporting data are available from ASTM Headquarters. Request RR: D19-1131.

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

TABLE 3 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 4 Final Statistical Summary for Cyanide Round Robin

	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

TEST METHOD B—CYANIDES AMENABLE TO CHLORINATION 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.

20.2 For the removal of these interferences, proceed as instructed in 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.

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.

NOTE 10—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.

TABLE 5 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

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 [7]

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.

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 5 and Table 6.

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.

27.2 For the removal of these interferences proceed as instructed in 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.

TABLE 6 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

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 [7]

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:

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	=	$0.092 + 0.02x$

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 7 and Table 8.

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 chemical compounds as listed in Section 6 can interfere.

34.2 For removal of these interferences, proceed as instructed in 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.

TABLE 7 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 8 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

34.6.1 For samples containing high concentrations of dissolved solids, 3 000 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 E 60. Spectrophotometers shall conform to Practice E 275.

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

36. Reagents and Materials

36.1 Refer to Section 8.

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 11.4 and 11.8. 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

TABLE 9 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

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.

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 [9]

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 9 and Table 10.

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 The distillation is performed following the method protocol on duplicate solutions containing known amounts of cyanide and duplicate blanks followed by the quantification procedure which will be used.

[9] Supporting data are available from ASTM Headquarters. Request RR: D19 – 1074.

TABLE 10 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

NOTE 11—With careful selection of concentration all four quantification procedures can be performed on the same distillate solution. (See Guide D 5788).

40.2.2 The recoveries should be 100 ± 10 % based on the verification data obtained for the quantifying procedures. The precision must be within the limits specified in the method for single operator standard deviation.

40.3 *Demonstration of Analyst Proficiency*:

40.3.1 Demonstrate the competence of the analyst before these methods are used to generate reportable work (See Section 9 of Practice D 5789).

40.3.2 Verify the procedure(s) to be used by analyzing cyanide standard solutions in the expected range.

40.3.3 Analyze in duplicate six samples of known or nearly the same concentration by the complete method expected to be used, such as distillation, chlorination, etc., plus colorimetric, electrode titration or ion chromatograph.

40.3.4 Calculate the standard deviation of the data in accordance with Guide D 3856 and Practices D 4210 and D 5789. If the value obtained is within the that given in the procedure for single operator precision, the analyst can be considered competent.

NOTE 12—If this is the first data generated in the laboratory, construct a preliminary control chart (see Guide D 3856 and Practice D 4210).

40.4 *Demonstration of Laboratory Proficiency*:

40.4.1 Analyze samples in duplicate until at least 40 data points are accumulated for each method or combination of methods used (see Section 5 of Practice D 4210).

40.4.2 Construct control charts with upper and lower limits from the data obtained (see Section 11 of Guide D 3856 and and Section 9 of Practice D 4210).

40.4.3 To monitor precision and bias analyze the following in duplicate: a standard solution, a sample of known value, a spiked sample, a field blank, and a method blank each day (or every 20 routine samples).

40.4.4 Calculate the relative range value (*R*) for each set of duplicate analyses. If the *R*s are greater than the upper control limit, the precision is judged out-of-control, and the analysis should be discontinued until the problem is resolved.

40.4.5 Calculate the percent recovery (*P*) for the standard and the spiked sample. If the recoveries are not within 100 ± 10 %, the analyses should be discontinued until the reason is found.

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.

APPENDIXES

(Nonmandatory Information)

X1. CYANIDE

X1.1 *Introductory Comments*—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 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

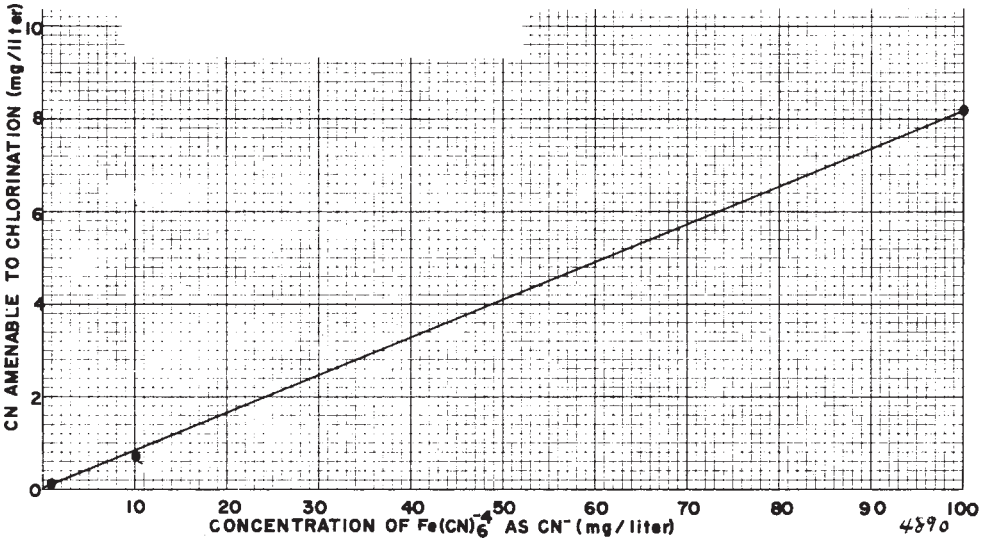

FIG. X1.1 Photodecomposition Rates for $Fe(CN)_6^{4}$ in Direct Sunlight, 20°C, pH 7, in Buffered Distilled Water, 75 mm Solution Layer, 1 h Exposure

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 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) 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 The distillation method, followed by the various analytical techniques to establish the quantitative cyanide content of the sample, has proven to be reliable. Extensive investigation and testing conducted in Germany has aided the evaluation of the recommended procedures **(34–40).** Cobalt

cyanide is not recovered completely during the distillation. The explanation for this condition was given by Leschber **(37)** and referred to by original investigations by Bassett and Corbet **(41).** 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 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.

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.

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

X1.9.3 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 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).**

X2. DETECTION AND ELIMINATION OF THE INTERFERENCE CAUSED BY ALDEHYDES

X2.1 Introductory Comments

X2.1.1 The inference caused by the presence of aldehydes, causing the conversion of cyanide to cyanohydrins has been explained in 11.3. Section 6.4 discusses the cyanohydrin formation when aldose is present in the sample. The same interference removal technique developed for the removal of the complexation caused by aldehydes may also be useful for the demasking of the complexes caused by the reaction with aldose. The aim is to recover the cyanide that is in a labile complex which also depends on the relative concentrations of the cyanide and complexing organics, the time past since the reacting chemical mixtures occurred, the temperature of the solution, and the organics present forming the various cyanohydrins.

X2.2 Summary of Methods

X2.2.1 *Silver Nitrate Method*—Formaldehyde present in the sample in excess of 0.5 mg/L noticeably interferes with the CN^- determination (0.02 mg CN^-/L). The cyanohydrin that is formed by the interaction of the cyanide and aldehyde in the sample is in equilibrium. This equilibrium is upset by the addition of silver nitrate which oxidizes the aldehyde to the noninterfering carboxylic acid prior to the cyanide determination. The EDTA solution complexes the iron, if present in the sample, to avoid the formation of iron cyanide.

X2.2.2 *Ethylene Diamine Method*—Ethylene diamine is a suitable demasking agent for the recovery of cyanide from labile cyanohydrins.

X2.3 Description of Spot Test

X2.3.1 E. Sawicki, et al, have developed a suitable colorimetric method for the detection and estimation of aliphatic aldehydes in water **(42–44).** This method has been adapted for a spot test procedure.

X2.4 Apparatus

X2.4.1 *Spot Plate*, white, with 6 to 12 cavities.

X2.5 Reagents and Materials

X2.5.1 *Ethylene Diamine Solution (3.5 %)*—Dilute 3.5 mL of pharmaceutical grade anhydrous $NH_2CH_2NH_2$ to 100 mL with water.

X2.5.2 *EDTA Solution* (0.1 *N*)—Dissolve 37.2 g of sodium-ethylenediamine-tetraacetate, dihydrated, in water and dilute to 1 L.

X2.5.3 *Ferric Chloride Oxidizing Solution*—Dissolve 1.6 g of sulfamic acid and 1 g of $FeCl_3 \cdot 6H_2O$ in 100 mL of water.

X2.5.4 *MBTH Indicator Solution*—Dissolve 0.05 g of 3-methyl, 2-benzothiazolone hydrochloride in 100 mL of water. Filter if turbid.

X2.5.5 *Silver Nitrate Solution (17 g/L)*—Dissolve 17 g of silver nitrate ($AgNO_3$) crystals in water and dilute to 1 L.

X2.6 Procedure

X2.6.1 If the sample is alkaline, add sulfuric acid (1 + 1) dropwise to 10 mL of the sample to adjust the pH to less than 8.0. Place 1 drop of sample and 1 drop of water for a blank in separate cavities of the spot plate. Add 1 drop of MBTH solution and then 1 drop of $FeCl_3$ oxidizing solution to each spot. Allow 10 min for color development. The color change will be from a fruit green-yellow to a deeper green with blue-green to blue at high concentrations of aldehyde. The blank should remain yellow. The sensitivity of the test is approximately 0.2 mg/L CH_2O.

X2.6.2 *Silver Nitrate Method*:

X2.6.2.1 Add $AgNO_3$ solution dropwise to the sample and retest on the spot plate. For each drop of $AgNO_3$ add also 2 drops of EDTA solution. One milligram CH_2O/100 mL of sample will require approximately 2 drops of $AgNO_3$ solution and 4 drops of EDTA solution.

X2.6.2.2 The silver nitrate may also precipitate some of the thiocyanate if present in the sample. If this should be avoided, add a few drops of concentrated ammonium hydroxide to the sample. In case $AgNO_3$ solution has been added in excess and it is found that AgCN has precipitated, ammonium hydroxide can be added subsequent to the CH_2O removal to resolubilize the CN^- and Ag^+. The dark precipitate that has formed is metallic silver and can be filtered off if turbidity interferes with the test method.

X2.6.3 *Ethylene Diamine Method*:

X2.6.3.1 Add 2 mL of the ethylene diamine solution for each 100 mL of sample to be used for the cyanide determination. It has been found that this quantity of ethylene diamine addition is suitable to overcome the interference caused by up to 50 mg/L CH_2O present.

X2.6.4 When applying a spike in testing or evaluation of the methods do not expect necessarily 100 % recovery of the CN^-. Recovery will depend on CH_2O excess that has been present, time of contact, and temperature of the sample.

REFERENCES

(**1**) Miller, J. C. and Miller, J. N., *Statistics for Analytical Chemistry*, 3rd ed., Ellis Horwood PTR Prentice Hall, 1993, pp. 124–129.

(**2**) Doudoroff, P., "Some Experiments on the Toxicity of Complex Cyanides to Fish," *Sewage and Industrial Wastes*, Vol 28, No. 8, August 1956, p. 1020.

(**3**) Doudoroff, P., Leduc, G., and Schneider, C. R.," Acute Toxicity to Fish of Solutions Containing Complex Metal Cyanides, in Relation to Concentrations of Molecular Hydrocyanic Acid," *Transactions of American Fisheries Society*, Vol 95, January 1966, p. 116.

(**4**) Wuhrmann, K., and Woker, H., *Schweizische Zeitschrift Fuer Hydrologie*, Vol 11, 1948, p. 210.

(**5**) Milne, D., "Disposal of Cyanides by Complexation," *Sewage and Industrial Wastes*, Vol 22, No. 9, September 1950, p. 1192.

(**6**) Schneider, C. R., and Freund, H., "Determination of Low Level Hydrocyanic Acid," *Analytical Chemistry*, Vol 34, 1962, p. 69.

(**7**) Claeys, R., and Freund, H., "Chromatographic Separation of HCN," *Environmental Science & Technology*, Vol 2, No. 6, June 1968, p. 458.

(**8**) Montgomery, H. A. C., et al., "Determination of Free Hydrogen Cyanide in River Water," *Analyst*, Vol 94, April 1969, p. 284.

(**9**) Nelson, K. H., and Lysyj, I., "Analysis of Water for Molecular Hydrogen Cyanide," *Journal of the Water Pollution Control Federation*, Vol 43, No. 5, May 1971, p. 799.

(**10**) Kruse, J. M., and Thibault, L. E., "Determination of Free Cyanide in Ferro- and Ferricyanides," *Analytical Chemistry*, Vol 45, 1973, p. 2260.

(**11**) Lancy, L., and Zabban, W., "Analytical Methods and Instrumentation for Determining Cyanogen Compounds," ASTM STP 337, ASTM 1962.

(**12**) Milne, D., "Equilibria in Dilute Cyanide Waste Solutions," *Sewage and Industrial Wastes*, Vol 22, No. 7, July 1950, p. 904.

(**13**) Anon, "Activities Report," *U. S. Department of Health Education Welfare*, July 1, 1963–June 30, 1964, p. 13.

(**14**) Backsteeg, W., and Thiele, H., *Gas and Wasserfach 98*, 1957, p. 909.

(**15**) Doudoroff, P., "Toxicity to Fish of Cyanides and Related Compounds," (A Review), (EPA-600/3-76-038, 1976 NTIS).

(**16**) Lancy, L., and Zabban, W., "Die Beziehung Zwischen Analyse und Behandlung von cyanidehaltigem Abwasser," Metalloberflache, Vol 13, No. 3, March 1963, p. 65.

(**17**) Ellis, M. M., "Detection and Measurement of Stream Pollution," U. S. Department of Commerce, Bureau of Fisheries, Bulletin No. 22, 1937, p. 427.

(**18**) Burdick, G. E., and Lipschuetz, M., "Toxicity of Ferro and Ferricyanide Solutions to Fish," *Transactions of American Fisheries Society*, Vol 78, 1948, p. 192.

(**19**) Lancy, L. E., and Fischer, G., "Die Bestimmung der durch alkalische Chlorbehandlung zerstörbaren Cyanide,"*Galvanotechnick*, Vol 59, No. 3, March 1968, p. 192.

(**20**) Schuster, H., and Winkel, P., "Cyanid Entgiftung," *Galvanotechnik*, Vol. 59, No. 3, March 1968, p. 189.

(**21**) Drew, D. M., "Simultaneous Determination of Ferrocyanide and Ferricyanide in Aqueous Solutions Using Infrared Spectrometry," *Analytical Chemistry*, Vol 45, 1973, p. 2423.

(**22**) Leschber, R., "Die Beurteilung der Toxizitat cyanidhaltiger Abwasser," *Galvanotechnik*, Vol 60, No. 5, May 1969, p. 368.

(**23**) Lancy, L. E., "Uber die Planung von Anlagen zur kontinuierlichen alkalischen Chlorierung cyanidhaltiger Abwasser," *Galvanotechnik*, Vol 49, No. 1, January 1958, p. 14.

(**24**) U. S. Patent 2 98 682 and 3 101 320.

(**25**) Doudoroff, P., and Katz, M., "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components of Fish," *Sewage and Industrial Wastes*, Vol 22, No. 11, November 1950, p. 1432.

(**26**) Zillich, J. A., "Toxicity of Combined Chlorine Residuals to Fresh Water Fish," *Journal of the Water Pollution Control Federation*, Vol 44, No. 2, February 1972, p. 212.

(**27**) Pettet, A. E. J., and Ware, G. C., "Disposal of Cyanide Wastes," *Chemistry and Industry*, Oct. 1, 1955, p. 1232.

(**28**) Bailey, P. L., and Bishop, E.," The Determination of Cyanogen Chloride," *Analyst*, Vol 97, September 1972, p. 691.

(**29**) Bailey, P. L., and Bishop, E., "Hydrolysis of Cyanogen Chloride," *Journal Chemical Society*, 1973, p. 912.

(**30**) Resnick, J. D., et al., "The Behavior of Cyanates in Polluted Water," *Industrial and Engineering Chemistry*, Vol 50, January 1958, p. 71.

(**31**) Dodge, B. F., and Zabban, W., "Analytical Methods for the Determination of Cyanates in Plating Wastes," *Plating*, Vol 39, No. 4, April 1952, p. 381.

(**32**) Gardner, D. C., "The Colorimetric Determination of Cyanates in Effluents," *Plating*, Vol 43, No. 6, June 1956, p. 743.

(**33**) "Procedures for Analyzing Metal Finishing Wastes," *Ohio River Valley Sanitation Commission*, 1954, p. 15–20.

(**34**) Leschber, R., "Verfahren zur Bestimmung von Cyaniden," *Galvanotechnik*, Vol 58, No. 7, July 1967, p. 462.

(**35**) Lancy, L. E., "Abwasserprobleme,"*Galvanotechnik*, Vol 58, No. 4, April 1967, p. 244.

(**36**) Weiner, Von R., and Leiss, Chr., "Kritische Untersuchungen zur Kolorimetrischen Cyanidbestimmung,"*Metalloberflache*, Vol 26, No. 6, June 1971, p. 185.

(**37**) Leschber, R., "Zur Frage des durch Chlorzerstobaren Cyanids," *Galvanotechnik*, Vol 59, No. 10, October 1968, p. 823.

(**38**) Leschber, R., and Schlichting, H., "Uber die Zersetzlichkeit komplexer Metallcyanide bie der Cyanidbestimmung in Abwasser," *Zeitschrift Analytische Chemie*, Vol 245, 1969, p. 300.

(**39**) Bucksteeg, W., and Dietz, F., "Zur Bestimmung und Beurteilung des Cyanides in Wasser," *Wasser Luft und Betrieb*, Vol 13, November 1969, p. 417.

(**40**) Bucksteeg, W., and Dietz, F., "Zur Bestimmung und Beurteilung des Cyanides in Wasser," *Wasser Luft und Betrieb*, Vol 13, December 1969, p. 475.

(**41**) Bassett, H., Jr., and Corbet, A. S., *Journal Chemical Society*, Vol 125, 1924, p. 1358.

(**42**) Sawicki, E., et al., "The 3-Methyl-2-Benzothiazolone Hydrazone Test Sensitive New Methods for the Detection, Rapid Estimation, and Determination of Aliphatic Aldehydes,"*Analytical Chemistry*, Vol 33, 1961, p. 93.

(**43**) Hauser, T. R., and Cummins, R. L., "Increasing Sensitivity of 3-Methyl-2-Benzothiazolone Hydrazone Test for Analysis of Aliphatic Aldehydes in Air," *Analytical Chemistry*, Vol 36, 1964, p. 679.

(**44**) Methods of Air Sampling and Analysis, 1st ed. 1972. Inter Society Committee, Air Pollution Control Association 199–204.