Designation: ~~D4282 – 02 (Reapproved 2015)~~ D4282 – 15

Standard Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion[1]

This standard is issued under the fixed designation D4282; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of free cyanides in waters and wastewaters. Free cyanide is here defined as the cyanide which diffuses as cyanide (HCN), at room temperature, from a solution at pH 6.[2]

1.2 This test method does not include complexes that resist dissociation, such as hexacyanoferrates and gold cyanide, nor does it include thiocyanate and cyanohydrin.

1.3 This test method may be applied to water and wastewater samples containing free cyanide from 10 to 150 µg/L. Greater concentrations may be determined by appropriate dilution.

1.4 This test method has been fully validated by collaborative testing as specified by Practice D2777.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.* For specific hazard statements, see 8.6, 8.9, Section 9, and 12.2.1.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[4]
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)[4]
D5788 Guide for Spiking Organics into Aqueous Samples
D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents (Withdrawn 2002)[4]
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 ~~*Definitions—*~~*Definitions:* ~~For a definition of terms used in this test method, refer to Terminology D1129.~~

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

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[2] The paper by J. M. Kruse and L. E. Thibault "Determination of Free Cyanide in Ferro- and Ferricyanides," Analytical Chemistry, 45(13): 2260–2261; 1973 Nov., recommends a diffusion at pH 7. The ANSI modification (ANSI PH 4.41-1978) uses pH 6. Using the conditions of the ANSI method, diffusion is completed within 4 hours at pH 6. Longer diffusion time was required at pH 7 on the samples analyzed.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The last approved version of this historical standard is referenced on www.astm.org.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *free cyanide*—~~refers to~~ those simple cyanides or loosely held cyanide complexes ~~of cyanide~~ that diffuse at pH 6, at room temperature.

4. Summary of Test Method

4.1 The reactions are carried out in a microdiffusion cell.

4.2 The sample is treated with cadmium ion to precipitate the hexacyanoferrates.

4.3 The sample is buffered at pH 6 and allowed to stand for 4 h.

4.4 The HCN diffuses into sodium hydroxide solution.

4.5 An aliquot of the sodium hydroxide solution is treated with chloramine-T, and the cyanogen chloride formed is reacted with barbituric acid in pyridine. The absorbance of the color formed is measured using a spectrophotometer at a wavelength of 580 nm.

5. Significance and Use

5.1 This test method is useful in distinguishing between the potentially available free cyanide (total cyanide) and the free cyanide actually present.

5.2 This test method provides a convenient technique for making on-site free cyanide determinations.

6. Interferences

6.1 *Decomposition of Hexacyanoferrates During Diffusion:*

6.1.1 This decomposition is virtually eliminated by allowing the sample to diffuse in the dark, and by precipitating the hexacyanoferrates with cadmium ion.

6.2 *Instability of Free Cyanide in Effluents*—The reactivity of free cyanide with such chemicals as aldehydes or oxidizing agents, is not really a method interference. However, because of this instability, it is important for the diffusion to begin as soon after sampling as possible. It is beyond the scope of this test method to list all the possible cyanide reactions that may be encountered.

7. Apparatus

7.1 *Diffusion Cell,* microdiffusion cell, Conway type, 68 mm outside diameter.[5]

7.2 *Micropipets,* 0.10 mL, 1.00 mL.

7.3 *Spectrophotometer,* conforming to Practice E275.

7.4 *Spectrophotometer Cell,* 1 cm equipped with a stopper.

7.5 *Pipet or Syringe,* adjustable (to deliver 1.30 mL).

7.6 *Calomel Reference Electrode,* with saturated KNO_3 electrolyte, or the equivalent.

7.7 *pH Meter.*

7.8 *Silver Electrode.*

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society[6] where such specifications are available. Other grades may be used provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

8.3 *Cadmium Chloride Solution* (10 g/L), $CdCl_2$—Dissolve 10.0 g of anhydrous cadmium chloride in 750 mL of water in a 1 L volumetric flask. Dilute to volume with water.

8.4 *Chloramine-T Reagent* (10 g/L)—Dissolve 1.00 g of chloramine-T in 50 mL of water in a 100 mL volumetric flask. Dilute to volume with water. Make this reagent fresh daily.

[5] One source of supply for these cells is Arthur H. Thomas, No. 3806-F-10.

[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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.5 *Cyanide Solution, Standard* (1.00 mL = 2 µg CN^-) —Pipet 2.00 mL of cyanide stock solution (approximately 1.0 g/L CN^-) into a 1 L volumetric flask and dilute to volume with sodium hydroxide solution (2.05 g/L).

8.6 *Cyanide Solution Stock*—Dissolve 2.51 g of potassium cyanide, KCN, in 500 mL of sodium hydroxide solution (2.05 g/L) in a 1 L volumetric flask. Dilute to volume with sodium hydroxide solution (2.05 g/L). This solution contains approximately 1.0 g/L cyanide (CN^-). (**Warning—**KCN is highly toxic, avoid contact or inhalation. Prepare and standardize this solution weekly.)

8.6.1 *Standardizing Cyanide Stock Solution:*

8.6.1.1 Using a silver electrode and a reference electrode, titrate 20.0 mL of the cyanide stock solution (in a beaker also containing 50 mL of sodium hydroxide solution (2.05 g/L)) with the silver nitrate standard solution.

8.6.1.2 Record the mL of titration for use in the calculation (see Fig. 1 for an example of a typical titration curve).

8.6.1.3 Calculate the concentration of the cyanide stock solution using the following equation:

$$50 \times (\text{mL silver nitrate}) = \text{mg/L } CN^- \text{ in stock solution}$$

1.00 mL of silver nitrate solution is equal to 1 mg of CN^-.

8.7 *Potassium Phosphate Buffer Solution (Acidified)*—Add 8.0 mL of concentrated phosphoric acid (sp gr 1.69), H_3PO_4, to 100 mL of potassium phosphate solution.

8.8 *Potassium Phosphate Solution*, 190 g/L—Add 400 mL of water to a 2 L beaker. Add and dissolve 14.5 g of sodium hydroxide, NaOH. Add and dissolve 190 g of potassium phosphate, monobasic, KH_2PO_4. Add water to 950 mL to aid dissolution. Adjust the pH of the solution to pH 5.9 to 6.1, using 100 g/L sodium hydroxide solution. Transfer the solution to a 1 L volumetric flask, and dilute to volume with water.

8.9 *Pyridine-Barbituric Acid Reagent*—Add 15.0 g of barbituric acid to a 250 mL volumetric flask. Wash down the sides of the flask with just enough water to moisten the barbituric acid. Add 75 mL of pyridine and swirl to mix. Slowly add 15 mL of concentrated hydrochloric acid (sp gr 1.19) and swirl to mix. Cool the solution to room temperature. Dilute to volume and mix. It is recommended that this reagent be prepared fresh weekly and stored in a dark place. (**Warning—**Pyridine is toxic; avoid contact or inhalation. Prepare this reagent in an exhaust hood.)

8.10 *Silver Nitrate Solution, Standard* (1 mL = 1 mg of CN^-)—Weigh 3.2647 g of silver nitrate on an analytical balance. Quantitatively transfer the silver nitrate to a 1 L volumetric flask. Dissolve and dilute to volume with water. Store in a dark glass bottle.

8.11 *Sodium Hydroxide Solution* (4.1 g/L), NaOH—Add 4.10 g of sodium hydroxide to 800 mL of water in a 1 L volumetric flask. Stir until dissolved, and cool the solution to room temperature before adjusting the final volume to 1 L.

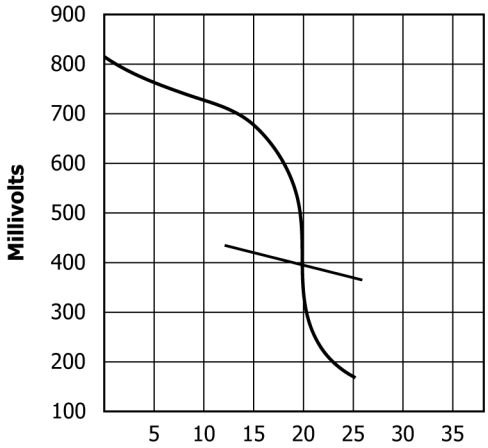
8.12 *Sodium Hydroxide Solution* (2.05 g/L), NaOH—Add 2.05 g of sodium hydroxide to 800 mL of water in a 1 L volumetric flask. Stir until dissolved, and cool the solution to room temperature before adjusting the final volume to 1 L. (An alternative preparation is to dilute 0.10 *N* sodium hydroxide solution with an equal volume of water.)

9. Hazards

9.1 *Safety Precautions:*

9.1.1 Because of the toxicity of cyanide, exercise great care in its handling. Acidification of cyanide solutions produces toxic gaseous hydrocyanide acid (HCN). Perform all manipulations in the hood so that any HCN that might volatilize is safely vented.

9.1.2 Some of the reagents used in these methods, such as cyanide solutions, are highly toxic. Dispose of these reagents and their solutions properly.



NOTE 1—Twenty millilitres of 2.51 g/L KCN titrated with $AgNO_3$.

FIG. 1 Typical Titration Curve Standardizing KCN Solution