Designation: D 4165 – 00

An American National Standard

Standard Test Method for Cyanogen Chloride in Water [1]

This standard is issued under the fixed designation D 4165; 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 cyanogen chloride in water. Cyanogen chloride is normally present only at very low concentrations; it is a very labile and sparsely soluble gaseous compound. Water samples may contain cyanogen chloride after the chlorination of waste waters containing cyanide or thiocyanate compounds.

1.2 Cyanogen chloride is unstable. A quick test using a spot plate or comparator as soon as the sample is collected may be the best test, reducing the loss of cyanogen chloride during the time lapse between sampling and analysis. (See Fig. 1 for a typical decay curve for cyanogen chloride in a solution.)

1.3 This test method has been used successfully with reagent water. The analyst is responsible for determining whether the test method is applicable to the water matrix being tested. Reference is made to Test Method D of Test Methods D 2036 which is based on similar chemical reactions and has been evaluated by collaborative testing in this matrix.

1.4 The lower limit of detectability is 0.005 mg CN^-/L.

1.5 *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 1 and Note 2 and Section 9.

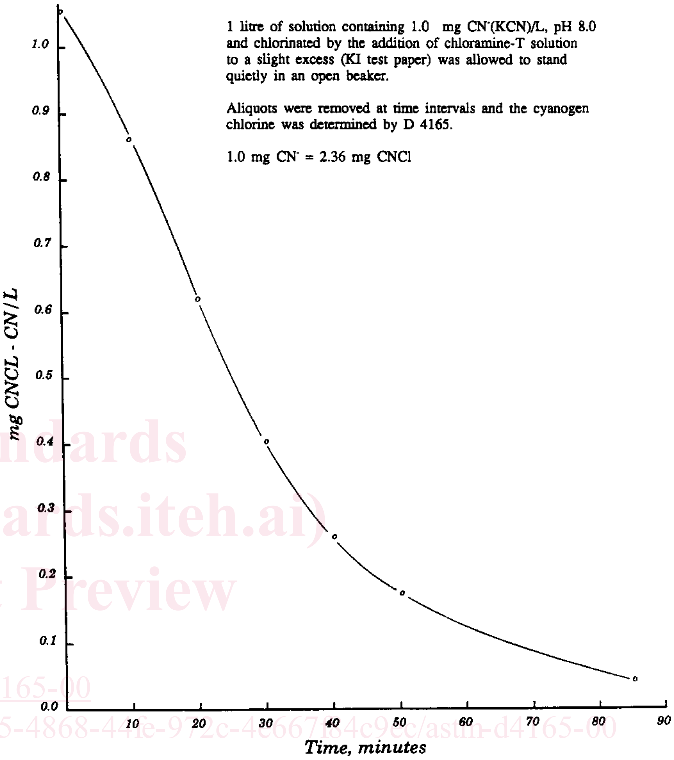

FIG. 1 Cyanogen Chloride Stability

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2036 Test Methods for Cyanides in Water[3]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]

D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]

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

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[2]

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 this test method, refer to Terminology D 1129.

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved June 10, 2000. Published July 2000. Originally published as D 4165 – 82. Last previous edition D 4165 – 95.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

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

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

4. Summary of Test Method

4.1 The water sample is mixed with a pyridine-barbituric acid solution and the color produced is measured with a spectrophotometer.

5. Significance and Use

5.1 The presence of cyanogen chloride in chlorinated sanitary and industrial effluents and therefore receiving waters is of concern because of its toxicity to aquatic life.

5.2 This test method provides an analytical procedure for measuring cyanogen chloride in water.

5.3 This test method is applicable for clean metal finishing and chlorinated sanitary and industrial effluents, and also can be used to establish process control of cyanide destruction by chlorination in waste water treatment facilities.

6. Interferences

6.1 Color and turbidity can interfere.

7. Apparatus

7.1 *Spectrophotometer or Filter Photometer*, suitable for measurement in the region of 578 nm, using 1.0-cm absorption cells. Filter photometers and photometric practices used in this test method shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275.

8. Reagents

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 Chem-ical 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 *Barbituric Acid*.

8.4 *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. Store in an amber bottle under refrigeration. Prepare fresh weekly.

8.5 *Cyanide Solution, Stock* (1 mL = 250 µg CN^-)—Dissolve 0.6258 g of potassium cyanide (KCN) in 40 mL of sodium hydroxide solution (40 g/L). Dilute to 1 L with water. Mix thoroughly; standardize with standard silver nitrate solution (see Section 8 of Test Methods D 2036).

NOTE 1—**Warning:** Because KCN is highly toxic, avoid contact or inhalation. Do not pipet by mouth (see Section 9).

8.5.1 *Cyanide Solution I, 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).

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

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

8.6 *Phosphate Buffer*— Dissolve 138 g of sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) in water and dilute to 1 L. Refrigerate this solution.

8.7 *Pyridine*.

NOTE 2—**Warning:** Pyridine may cause irritation to the skin and respiratory tract. Do not pipet by mouth (see Section 9).

8.8 *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.

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

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

9. Hazards

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

9.2 **Warning:** Many of the reagents used in this test method are highly toxic. These reagents and their solutions must be disposed of properly (such as potassium cyanide and pyridine).

10. Sampling and Sample Preservation

10.1 Collect the sample in accordance with Practices D 3370.

10.2 Collect a separate sample in a closed container. DO NOT ADD NaOH, as cyanogen chloride will be hydrolyzed to cyanate at pH 12 or more. As soon as possible after collection, analyze in accordance with Section 12. If the sample should be preserved and the pH is high, reduce the pH to the 8.0 to 8.5 range with careful additions of phosphate buffer when the sample is collected, and immediately cool to 4°C.

11. Standardization

11.1 Prepare a series of cyanide standard solutions by pipetting aliquots of cyanide Solution III into 50-mL volumetric flasks (see Note 1). Dilute to approximately 20 mL with NaOH solution (1.6 g/L).

NOTE 3—Aliquots should cover the concentration range expected in the samples.

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[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.