Designation: D4193 – 08 (Reapproved 2020)ε1

Standard Test Method for Thiocyanate in Water[1]

This standard is issued under the fixed designation D4193; 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.

ε[1] NOTE—Warning notes were editorially updated throughout in January 2020.

1. Scope

1.1 This test method covers the quantitative colorimetric laboratory measurement of dissolved thiocyanate in water, waste water, and saline water in the range from 0.1 to 2.0 mg/L. For higher concentrations, use an aliquot from the diluted sample.

1.1.1 *Validation*—This test method was validated over the range of 0.07 to 1.42 mg/L. This test method was validated at nine laboratories at four levels. This test method may be valid for reporting results down to lower levels as validated in individual user laboratories.

1.1.2 *Application*—This test method has been validated in reagent water, Type II, in multiple laboratories and 7 natural waters, 1 laboratory effluent, 1 steel mill effluent, and 2 dechlorinated and treated sanitary effluents in single laboratories. It is the user's responsibility to assure the validity of the test method on any untested matrices.

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

1.3 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 9.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]

D1193 Specification for Reagent Water

D2036 Test Methods for Cyanides in Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3370 Practices for Sampling Water from Flowing Process Streams

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)[3]

D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents

D5788 Guide for Spiking Organics into Aqueous Samples

D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents (Withdrawn 2002)[3]

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D7237 Test Method for Free Cyanide and Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

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

[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] 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.

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

3. Terminology

3.1 *Definitions:*

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

4. Summary of Test Method

4.1 This test method consists of thiocyanate reacting with ferric ions at a pH of <2 to form a colored complex which is determined colorimetrically at 460 nm and adheres to Beer's Law.

4.2 Industrial wastes may be highly colored and contain various interfering organic compounds which must be removed by adsorption on macroreticular resin[4] prior to analysis.

5. Significance and Use

5.1 This test method is useful for analysis of many natural waters that contain thiocyanate from organic decomposition products and waste water discharges. Some industrial wastes, such as those from the metallurgical processing of gold ores, steel industry, petroleum refining, and coal gasification, may contain significant concentrations of thiocyanate. Thiocyanate per se is not recognized as a toxic chemical compound. However, when chlorinated, thiocyanate is converted to the highly toxic and volatile cyanogen chloride at high pH. Oxidation of thiocyanate may also release toxic hydrogen cyanide. The user of the method is advised to perform holding time studies in accordance with Practice D4841 whenever oxidants are present in the samples.

5.1.1 For information on the impact of cyanogens and cyanide compounds, see Appendix X1 of Test Methods D2036.

6. Interferences

6.1 Hexavalent chromium interference is removed by adjusting the pH to 2 with concentrated nitric acid and adding ferrous sulfate. Raising the pH to 8.5–9 with sodium hydroxide precipitates Fe (III) and Cr (III) as the hydroxides, which are removed by filtration.

6.2 Reducing agents that reduce Fe (III) to Fe (II), thus preventing formation of the ferric thiocyanate complex, are destroyed by a few drops of hydrogen peroxide.

6.3 High concentrations of cyanide in proportion to the concentration of thiocyanate will react with the iron to form colored complexes.

6.4 Colored or interfering organic compounds must be removed by adsorption on macroreticular adsorption resin prior to analysis.

NOTE 1—Examples of interfering compounds are fluoride, phosphate, oxalate, arsenate, tartrate, borate, etc. which form complexes with iron.[5] Production of a red color with ferric ions is typical of phenols, enols, oximes, and acetates.[6]

6.5 Oxidation of thiocyanate may also react to form cyanides, resulting in low results. The user of the method is advised to perform holding time studies in accordance with Practice D4841 whenever oxidants are present in the samples.

6.6 Removal of sulfides for cyanide analysis preservation may result in reaction of cyanide to form thiocyanate. Use a separate sample for thiocyanate analysis than the one preserved for cyanide analysis.

7. Apparatus

7.1 *Spectrophotometer or Filter Photometer,* suitable for absorbance measurements at 460 nm and using a 5-cm cell. Filter photometers and photometric practices used in this test method shall conform to Practice E60. Spectrophotometers shall conform to Practice E275.

7.2 *Column*—Chromatographic, glass, 12-mm inside diameter by 600-mm length, equipped with a reservoir and stopcock, or a 50-mL buret with a glass wool plug and a funnel attached with a short piece of tubing.

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.[7]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I or II, and demonstrated to be free of specific interference for the test being performed.

8.3 *Acetone.*

8.4 *Ferric Nitrate Solution* (404 g/L)—Dissolve 404 g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in about 800 mL of water. Add to this solution 80 mL of concentrated nitric acid. Mix and dilute to 1 L with water.

8.5 *Hexane.*

8.6 *Hydrogen Peroxide Solution*—(H_2O_2), 30 %.

8.7 *Macroreticular Resin,*[8] 18- to 50-mesh or equivalent.

8.8 *Methyl Alcohol.*

8.9 *Nitric Acid*—Concentrated HNO_3, sp gr 1.42.

8.10 *Nitric Acid (0.1 M)*—Mix 6.4 mL of concentrated nitric acid in about 800 mL of water. Dilute to 1 L with water and mix.

8.11 *Thiocyanate Solution, Stock* (1 mL = 1.0 mg SCN^-)—Dissolve 1.673 g of potassium thiocyanate (KSCN) in water and dilute to 1 L.

[4] Spencer, R. R., Leenheer, J., and Marti, V. C., "Automated Colorimetric Determination of Thiocyanate, Thiosulfate, and Tetrathionate in Water," AOAC 94th Annual Meeting, Washington, DC, 1980.

[5] Newman, A. A. (ed.), *Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*, Academic Press, New York, NY, 1975.

[6] Shriner, R. L., and Fuson, R. C., *Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, NY, 1948.

[7] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

[8] For the development of this test method, Amberlite XAD-8 has been used. Amberlite is a trademark of the Rohm and Haas Co., Independence Mall West, Philadelphia, PA 19105.

8.12 *Thiocyanate Solution, Standard* (1 mL = 0.01 mg SCN^{-1})—Dilute 10 mL of the stock thiocyanate solution to 1 L with water. Prepare fresh for each use. See 10.4.

8.13 *Sodium Hydroxide Solution* (4 g/L)—Dissolve 4 g of NaOH in about 800 mL of water. Mix and dilute to 1 L with water.

9. Precautions

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

9.2 Residual sample remains could be toxic; these should be disposed of properly.

10. Sampling

10.1 Collect the sample in accordance with Guide D1192 and Practices D3370.

10.2 Thiocyanate is stable in both the acid and alkaline pH range.

10.3 If the sample is to be preserved for cyanide, remove the sulfide before stabilization at a high pH in accordance with Practice D7365 as follows: Treat the sample immediately using any or all of the following techniques as necessary, followed by adjustment of the sample to pH 12–13 and refrigeration.

10.3.1 *Sulfide*—Test for the presence of sulfide by placing a drop of sample on a lead acetate test strip that has been previously moistened with acetate buffer. If the test strip turns black, sulfide is present (above 50 mg/L S2-) and treatment is necessary as described in 10.3.1.1 or 10.3.1.2. If the test is negative and there are no further interferences suspected, adjust the pH to 12–13, refrigerate, and ship or transport to the laboratory.

10.3.1.1 If the sample contains sulfide as indicated with a lead acetate test strip or is known to contain sulfides that will interfere with the test method, dilute the sample with reagent water until the lead acetate test strip no longer indicates the presence of sulfide (<50 mg/L S2-) or until the interference is no longer significant to the analytical test method. For example, add 200 mL of freshly collected sample into a bottle containing 800 mL of reagent water, then test for sulfide again as indicated in 10.3.1. If the test for sulfide is negative, adjust the pH to 12–13, refrigerate, and ship or transport to the laboratory. If the test for sulfide is still positive, further dilution is required; however, be careful not to over dilute the sample as the detection limit will be elevated by this factor. In the aforementioned example, the dilution factor would be equal to 5 (total volume/sample volume). Clearly indicate the dilution volumes on the sample and chain-of-custody form so that the laboratory can mathematically correct the result.

10.3.1.2 Alternatively, sulfide can be removed by precipitation if free cyanide is the only form of cyanide to be measured (Test Method D7237). For removal of sulfide by precipitation, if the pH is less than pH 11, raise the pH to 11 with NaOH solution, and then add approximately 1 mg of powdered cadmium chloride for each ml of sample. Cap and shake the container to mix. Allow the precipitate to settle and test the sample with lead acetate paper for residual sulfide. If necessary, add more cadmium chloride but avoid adding excess. Finally filter through a 0.45-μm filter. Refrigerate, then transport or ship the filtrate to the laboratory.

NOTE 2—Some analytical methods prescribe the use of lead carbonate or lead acetate to precipitate sulfide; however, sulfide and cyanide can form thiocyanate in the presence of lead causing decreased cyanide recoveries; therefore, lead carbonate and lead acetate should be avoided. Methods that specify the addition of bismuth nitrate to treat sulfide during total cyanide distillations have been demonstrated by ASTM committee D19.06 to be ineffective.

(**Warning—**Cyanide can be converted into thiocyanate in the presence of sulfide at a high pH, causing high results.)

10.4 Thiocyanate is biodegradable. Samples that may contain bacteria should be preserved at pH <2 by the addition of mineral acid and refrigerated.

11. Preparation of Apparatus

11.1 *Resin Column*—Measure out sufficient resin to fill the column or columns into a beaker and add five times the resin volume of acetone. Stir for 1 h with gentle agitation.

11.2 Pour off the fines and the acetone from the settled resin and add five times the resin volume of hexane. Stir for 1 h.

11.3 Pour off any fines that may be present and the hexane from the settled resin and add five times the resin volume of methanol. Stir for 15 min.

11.4 Pour off the methanol from the settled resin and add three times the resin volume of NaOH solution (4 g/L). Stir for 15 min.

11.5 Pour off the NaOH solution from the settled resin and add three times the resin volume of 0.1 *M* HNO_3. Stir for 15 min.

11.6 Pour off the HNO_3 solution from the settled resin and add three times the resin volume of reagent water. Stir for 15 min. Decant the water from the settled resin and use this purified resin to fill the column.

11.7 Attach the tip of the column to a source of reagent water, and displace the air from the column with water to the bottom of the reservoir (tip of the funnel if a buret is used).

11.8 Add the resin slurry to the reservoir (funnel) and allow it to fill the column by displacing the water to approximately 400-mm depth. This procedure will give a uniform column with the correct degree of packing.

11.9 When the resin has settled allow the water to drain to the top of the resin bed. At no time should the liquid level be below the top of the resin bed.

11.10 Add and drain five 5-mL increments of sample solution to the column. Fill the reservoir (funnel) with the remaining (125 mL) solution and allow it to pass through the column at a rate of 20 mL/min. Discard the first 50 mL of eluate.

11.11 Collect the next 50 mL of eluate in a clean, dry, graduated cylinder. Use this portion for color development.