



Designation: D 4193 – 02

Standard Test Method for Thiocyanate in Water¹

This standard is issued under the fixed designation D 4193; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers the determination 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.

1.2 This test method has been used successfully with reagent grade, natural, and treated sanitary effluent waters. It is the user's responsibility to assure the validity of the test method on any untested matrices.

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water²

D 1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits²

D 1193 Specification for Reagent Water²

D 2036 Test Methods for Cyanides in Water³

D 3370 Practices for Sampling Water from Closed Conduits²

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water²

D 4210 Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data²

D 5788 Guide for Spiking Organics into Aqueous Samples³

D 5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents³

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis³

E 60 Practice for Molecular Absorption Spectrometric Methods for Chemical Analysis of Metals, Ores, and Related Materials⁴

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers⁵

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

4. Summary of Test Method

4.1 Thiocyanate reacts 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 resin⁶ prior to analysis.

5. Significance and Use

5.1 Many natural waters contain thiocyanate from organic decomposition products and waste water discharges. Some industrial wastes, such as those from the 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.

5.1.1 For information on the impact of cyanogen compounds, see Appendix X1 of Test Method D 2036.

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

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.

Current edition approved July 10, 2002. Published August 2002. Originally published as D 4193 – 82. Last previous edition D 4193 – 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.

⁶ 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.

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.⁷ Production of a red color with ferric ions is typical of phenols, enols, oximes, and acetates.⁸

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 E 60. Spectrophotometers shall conform to Practice E 275.

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.⁹

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

8.3 *Acetone*.

8.4 *Ferric Nitrate Solution (404 g/L)*—Dissolve 404 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) 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*¹⁰, 18- to 50-mesh or equivalent.

8.8 *Methyl Alcohol*.

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

⁷ Newman, A. A. (ed.), *Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*, Academic Press, New York, NY, 1975.

⁸ Shriner, R. L., and Fuson, R. C., *Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, NY, 1948.

⁹ *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.

¹⁰ 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.

8.10 *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.

8.12 *Thiocyanate Solution, Standard (1 mL = 0.01 mg SCN^-)*—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. Hazards

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 Specification D 1192 and Practices D 3370.

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 (see section 10.3.2 of Test Methods D 2036). Cyanide can be converted into thiocyanate in the presence of sulfide at a high pH.

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 and Use of Resin Column

11.1 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).