INTERNATIONAL

Designation: D 4193 – ~~95~~02

Standard Test Method for Thiocyanate in Water [1]

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 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 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:*

---

[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 ~~Sept.~~ July 10, ~~1995.~~ 2002. Published ~~November 1995.~~ August 2002. Originally published as D 4193 – 82. Last previous edition ~~D 4193 – 89 (1994)$^{\epsilon 1}$.~~ D 4193 – 95.

D 1129 Terminology Relating to Water[2]
D ~~1192 Specification~~ 1192 Guide for Equipment for Sampling Water and Steam~~.~~ in Closed Conduits[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 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]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]
E 60 Practice for ~~Photometric and Spectrophotometric~~ Molecular Absorption Spectrometric Methods for Chemical Analysis of Metals~~.~~, Ores, and Related Materials[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.

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 resin[6] 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 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.

---

[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 ~~14.01.~~ 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.

[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.

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 ($Fe(NO_3)_3 \cdot 9H_2O$) 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*[10], 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.

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. 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).

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.

---

[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.

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.

11.12 Drain any remaining solution to the top of the resin bed. Regenerate the resin by the serial addition of five 5-mL and one 75-mL portions of NaOH solution (4 g/L), five 5-mL and one 25-mL portions of 0.1 *M* HNO_3 and five 5-mL and one 75-mL portions of water. If the flow rate has reduced to 4 to 5 mL/min, it is advisable to rinse the resin with 100 mL of methanol or backwash by introducing water into the bottom of the column and allowing it to escape at the top, or use both procedures. The rate of backwashing should be rapid enough to expand the bed, but not allow loss of the resin.

12. Standardization

12.1 Prepare a series of thiocyanate standards containing 0.0 to 2.0 mg SCN^-/L by pipetting 0-(blank) to 40-mL aliquots of standard thiocyanate solution into 200-mL volumetric flasks. Dilute to volume with water and mix thoroughly.

12.2 Follow 13.1-13.3 of the procedure.

NOTE 2—If it has been established that the sample contains no interfering compounds, the use of the absorption column can be eliminated from both the standardization and sample procedures.

12.3 Calculate the slope and intercept of the curve. See 14.1.1.

13. Procedure

13.1 Acidify 150 mL of sample (or an aliquot of sample diluted to 150 mL) to pH 2 by the dropwise addition of concentrated nitric acid and pass it through the resin column at a flow rate not exceeding 20 mL/min. (See 11.10-11.12.)

13.2 Pour the 50 mL of collected eluate into a beaker, add 2.5 mL of ferric nitrate solution, and mix.

13.3 Within 5 min., determine the absorbance of the solution at 460 nm in a 5.0-cm cell using water as a reference.

14. Calculation

14.1 Calculate the concentration of thiocyanate (SCN) in milligrams per litre as follows:

14.1.1 *Slope and Intercept of Standard Curve*:

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

$$\text{Intercept on } c \text{ axis, } b = \frac{\Sigma a^2\Sigma c - \Sigma a\Sigma ac}{n\Sigma a^2 - (\Sigma a)^2}$$

where:

a = absorbance of standard solution,
c = concentration of SCN in standard solution, and
n = number of standard solution.

14.2 *Concentration*:

$$\text{SCN, mg/L} = (ma^1 + b) \times (\text{dilution factor, if any})$$

where:

a^1 = absorbance of sample solution,
b = intercept on c axis, and
m = slope of standard curve.

15. Precision and Bias [11]

15.1 *Precision*—Based on the results of 12 operators and 9 laboratories conducting tests on four levels of concentration, the precision of the test method within its designated range is linear with concentration and may be expressed as follows:

Reagent Water: $S_t = 0.093x + 0.0426$
$S_o = 0.045x + 0.010$
Water matrix: $S_t = 0.055x + 0.0679$
$S_o = 0.024x + 0.0182$

where:

---

[11] 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.

S_t = overall precision, mg/L,
S_o = pooled single-operator precision, mg/L, and
x = concentration of thiocyanate, mg/L.

15.2 *Bias*—Recoveries of known amount of thiocyanate from reagent water, Type II, 7 natural waters, 1 laboratory effluent, 1 steel mill effluent, and 2 dechlorinated and treated sanitary effluents were as shown in Table 1.

15.2.1 For other matrices, these data may not apply.

16. Quality Assurance/Quality Control

16.1 Before this test method is applied to the analysis of samples of unknown thiocyanate concentration, the analyst must establish quality control by the procedures recommended in Practice D 4210 and Guide D 3856.

16.2 A duplicate sample and known standard must be analyzed each day that an analysis is performed. The duplicate and standard shall meet the limits as established by the control chart before a determination is considered satisfactory.

16.3 A blank and a spiked sample shall be analyzed each day that an analysis is performed. Spiking shall be in accordance with that outlined in ~~Guide D 3856 (11.11).~~ D 3856, D 5788 and D 5789. The blank shall be low enough that it will not unduly influence the data.

16.4 One sample must be analyzed in duplicate with each group of 10 or less samples. The results must meet the limits established in Section 15 of this test method before the data for that batch or set of 10 samples are acceptable.

~~16.5 Other QA/QC portions~~

16.5 *Demonstration of Analyst Proficiency*

16.5.1 Demonstrate the competence of the analyst before this ~~test~~ method ~~have not been completely established at this time. Analysts performing this test method will be required~~ is used to ~~measure their performance against~~ generate reportable data (Practice D 5789, Section 9).

16.5.2 Verify the ~~performance level achieved~~ procedure to be used by analyzing standard solutions in the ~~interlaboratory study~~ expected range.

16.5.3 Analyze in duplicate six samples of ~~this test~~ known or nearly the same concentration by the method.

16.~~6~~5.4 Calculate the standard deviation of the data (D 3856, D 4210, D 5789, and D 5847). If the value obtained is within that given in the procedure for single operator precision, the analyst can be considered "competent" (Note 3).

NOTE 3—If this is the first data generated in the laboratory, construct a preliminary control chart (D 3856, D 4210).

16.6 *Demonstration of ~~Subcommittee D19.06~~ Laboratory Proficiency*

16.6.1 Initially analyze five or six samples in duplicate to ~~incorporate formal QA/QC procedures into this test~~ obtain a crude estimate of population standard deviation. If the method is used routinely, continue to accumulate additional data until at ~~such time as they have passed~~ least 40 data points are obtained (D 4210, Section 5).

16.6.2 Construct a control chart with upper and lower limits from the ~~consensus process~~ data obtained (D 3856, Section 11 and ~~have been officially accepted by~~ D 4210, Section 9).

16.6.3 To monitor precision and bias, analyze the ~~S~~ following in duplicate: a standard solution, a sample of known value, a spiked sample (D 5788), a field blank, and a method blank each day (or every 20 routine samples).

16.6.4 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 analyses should be discontinued until the problem is resolved.

16.6.5 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.

17. Keywords

17.1 cyanide; cyanogen chloride; ferric ions; macroreticular resin (XAD-8); spectrophotometer; thiocyanate

TABLE 1 Bias for Thiocyanate Test Method

Amount Added, mg/L	Amount Found, mg/L	n	S_T	S_O	Bias	% Bias	Statistically Significant (95 % Confidence Level)
				Reagent Water			
1.42	1.411	30	0.181	0.080	−0.009	−0.6	no
0.71	0.683	27	0.091	0.027	−0.027	−4	no
0.35	0.329	30	0.084	0.029	− 0.021	−6	no
0.07	0.068	30	0.052	0.018	− 0.002	−3	no
				Selected Water Matrices			
1.42	1.408	26	0.151	0.046	−0.012	−0.8	no
0.71	0.668	29	0.096	0.051	−0.042	−6	yes
0.35	0.320	29	0.085	0.025	− 0.030	−9	no
0.07	0.050	29	0.079	0.014	− 0.020	−29	no