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# 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 June 2013.

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

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D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]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

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, 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.

[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.

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 Method 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.

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.

[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] *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] 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.

## 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 Specification 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 Practices 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 Sections 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.

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. Calibration and 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 Acidify 150 mL of standard (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).

NOTE 3—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 Pour the 50 mL of collected eluate into a beaker, add 2.5 mL of ferric nitrate solution, and mix.

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

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

12.6 A duplicate sample and known standard must be analyzed each day that an analysis is performed.

12.7 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 D3856, D5788 and D5789. The blank shall be low.

12.8 One sample must be analyzed in duplicate with each group of 10 or fewer samples.

## 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:*

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

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

where:

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

14.2 *Concentration:*

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

where:

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

## 15. Precision and Bias[9]

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:

$$\begin{aligned} \text{Reagent Water: } S_t &= 0.093x + 0.0426 \\ S_o &= 0.045x + 0.010 \\ \text{Water matrix: } S_t &= 0.055x + 0.0679 \\ S_o &= 0.024x + 0.0182 \end{aligned}$$

where:

$S_t$ = 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

[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1099. Contact ASTM Customer Service at service@astm.org.

**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 |

sanitary effluents were as shown in Table 1. All laboratories analyzed reagent water and the other water matrices differed in each laboratory.

15.2.1 For other matrices, these data may not apply.

15.3 Nine independent laboratories (and a total of twelve operators) participated in the round-robin study. Precision and bias for this test method conforms to Practice D2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D2777-86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

## 16. Quality Assurance/Quality Control

16.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test:

16.2 *Calibration and Calibration Verification:*

16.2.1 *Instrument:*

16.2.1.1 Analyze at least five calibration standards containing 0–2 mg/L of thiocyanate prior to analysis of samples to calibrate the instrument.

16.2.1.2 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 D4210 and Guide D3856.

16.2.2 Verify instrument calibration after ten samples by analyzing a standard at the concentration of one of the calibration standards.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

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 D3856, D5788 and D5789. 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 fewer 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 *Demonstration of Analyst Proficiency:*

16.5.1 Demonstrate the competence of the analyst before this method is used to generate reportable data (Practice D5789, Section 9).

16.5.2 Verify the procedure to be used by analyzing standard solutions in the expected range.

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

16.5.4 Calculate the standard deviation of the data (D3856, D4210, D5789, and D5847). If the value obtained is within that given in the procedure for single operator precision, the analyst can be considered "competent" (Note 4).

NOTE 4—If this is the first data generated in the laboratory, construct a preliminary control chart (D3856, D4210).

16.6 *Initial Demonstration of Laboratory Proficiency:*

16.6.1 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

16.6.2 Initially analyze five or six samples in duplicate to obtain a crude estimate of population standard deviation. If the method is used routinely, continue to accumulate additional data until at least 40 data points are obtained (D4210, Section 5).

16.6.3 Construct a control chart with upper and lower limits from the data obtained (D3856, Section 11 and D4210, Section 9).

16.7 *Laboratory Control Sample (LCS):*

16.7.1 To ensure that the test method is in control, analyze an LCS in duplicate and a standard solution. The LCS must be taken through all of the steps of this analytical method including sample preservation and pretreatment.

16.7.2 Calculate the relative range value (R) for each set of duplicate analyses. If the Rs are greater than the upper control limit, the precision is judged out of control, and analyses should be discontinued until the problem is resolved.

16.7.3 Calculate the percent recovery (P) for the standard and the spiked sample. If the recoveries are not within 100 ± 10 %, analysis of samples is halted until the problem is corrected, and either all samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.8 *Method Blank (Blank)*

16.8.1 Analyze a reagent water test blank in duplicate with each batch. The concentration of thiocyanate found in the blank must be less than 0.01 mg/L. If the concentration of the thiocyanate is found above this level, analysis of samples is halted until the contamination is eliminated and blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.9 *Matrix Spike (MS):*

16.9.1 To check for interferences in the specific matrix being tested, perform an MS in duplicate on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of thiocyanate which is <1 mg/L thiocyanate and taking it through the analytical method.

16.9.2 The spike concentration plus the background concentration of thiocyanate must not exceed 1 mg/L thiocyanate. The spike must produce a concentration in the spiked sample 2 to 5 times the background concentration or 10 to 50 times the detection limit of the test method, whichever is greater.

16.9.3 Calculate the percent recovery of the spike (p) using the following formula:

$$P = \frac{100[A(V_s+V) - (B \times V_s)]}{C \times V}$$

where:

$A$ = concentration found in spiked sample,
$B$ = concentration found in unspiked sample,

$C$ = concentration of analyte in spiking solution,
$V_s$ = volume of sample used, and
$V$ = volume of spiking solution added.

16.9.4 Calculate the relative range value (R) for each set of duplicate analyses. If the Rs are greater than the upper control limit, the precision is judged out of control, and analyses should be discontinued until the problem is resolved.

16.9.5 Calculate the percent recovery (P) for the standard and the spiked sample. If the recoveries are not within 100 ± 10 %, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.10 *Duplicate:*

16.10.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch.

16.10.2 Calculate the standard deviation of the duplicate values and compare to the single operator precision in the collaborative study using an F test. Refer to 6.4.4 of Test Method D5847 for information on applying the F test.

16.10.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.11 *Independent Reference Material (IRM):*

16.11.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample in duplicate to the laboratory each day. The concentration of the reference material should be in the range of 0.05 mg/L thiocyanate to 2 mg/L of thiocyanate. The value obtained must fall within the control limits specified by the outside source.

## 17. Keywords

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