Designation: D6994 – 15

Standard Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection[1]

This standard is issued under the fixed designation D6994; 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 the metal cyanide complexes of iron, cobalt, silver, gold, copper and nickel in waters including groundwaters, surface waters, drinking waters and wastewaters by anion exchange chromatography and UV detection. The use of alkaline sample preservation conditions (see 10.3) ensures that all metal cyanide complexes are solubilized and recovered in the analysis (**1-3**).[2]

1.2 Metal cyanide complex concentrations between 0.20 to 200 mg/L may be determined by direct injection of the sample. This range will differ depending on the specific metal cyanide complex analyte, with some exhibiting greater or lesser detection sensitivity than others. Approximate concentration ranges are provided in 12.2. Concentrations greater than the specific analyte range may be determined after appropriate dilution. This test method is not applicable for matrices with high ionic strength (conductivity greater than 500 meq/L as Cl) and TDS (greater than 30 000 mg/L), such as ocean water.

1.3 Metal cyanide complex concentrations less than 0.200 mg/L may be determined by on-line sample preconcentration coupled with anion exchange chromatography as described in 11.3. This range will differ depending on the specific metal cyanide complex analyte, with some exhibiting greater or lesser detection sensitivity than others. Approximate concentration ranges are provided in 12.2. The preconcentration method is not applicable for silver and copper cyanide complexes in matrices with high TDS (greater than 1000 mg/L).

1.4 The test method may also be applied to the determination of additional metal cyanide complexes, such as those of platinum and palladium. However, it is the responsibility of the user of this standard to establish the validity of the test method for the determination of cyanide complexes of metals other than those in 1.1.

1.5 The presence of metal complexes within a sample may be converted to Metal CN complexes and as such, are altered with the use of this method. This method is not applicable to samples that contain anionic complexes of metals that are weaker than cyanide complexes of those metals.

1.6 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.7 *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, refer to Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent 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
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6696 Guide for Understanding Cyanide Species

3. Terminology

3.1 *Definitions:*

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

3.2 *Definitions of Terms Specific to This Standard:*

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Oct. 1, 2015. Published October 2015. Originally approved in 2004. Last previous edition approved in 2010 as D6994 – 10. DOI: 10.1520/D6994-15.

[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] 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.

***A Summary of Changes section appears at the end of this standard**

3.2.1 *anion exchange chromatography, n*—a type of liquid chromatography in which anionic analytes are separated by differential retention on an anion exchange resin and detected by an appropriate detection mechanism.

3.2.2 *eluent, n*—the liquid mobile phase used in anion exchange chromatography to transport the sample through the chromatography system.

3.2.3 *analytical column, n*—the chromatography column that contains the stationary phase for separation by ion exchange.

3.2.3.1 *Discussion*—The column is packed with anion exchange resin that separates the analytes of interest based on their retention characteristics prior to detection.

3.2.4 *guard column, n*—a short chromatography column that is placed before the analytical column to protect the latter from particulates and impurities that may cause fouling.

3.2.5 *anion trap column, n*—a high-capacity, low-pressure anion exchange column used to remove reagent impurities from the eluent stream.

3.2.5.1 *Discussion*—The anion trap column is placed between the eluent reservoir and the gradient pump.

3.2.6 *gradient elution, n*—a type of elution in which the eluent composition is steadily altered throughout the analysis in order to provide for an adequate separation of the analytes of interest prior to detection.

3.2.7 *gradient pump, n*—a liquid chromatography pump that is capable of performing gradient elutions.

3.2.8 *total cyanide, n*—the sum total of all of the inorganic chemical forms of cyanide.

3.2.8.1 *Discussion*—Total cyanide thus includes both free cyanide and anionic metal cyanide complexes.

3.2.9 *metal cyanide complex, n*—a negatively charged ionic complex consisting of one or more cyanide ions bound to a single transition metal cation.

3.2.9.1 *Discussion*—Also referred to as *metal-complexed cyanides*, these complexes have the general formula:

$$[M(CN)_b]^{x-} \quad (1)$$

where:

M = transition metal cation,
b = number of cyanide groups, and
x = ionic charge of the transition metal complex.

3.2.9.2 *Discussion*—Metal cyanide complexes are relatively stable and require moderate to highly acidic conditions in order to dissociate and form free cyanide. Based on their stability, metal cyanide complexes are divided into two categories: “weak metal cyanide complexes” and “strong metal cyanide complexes.” Examples of strong metal cyanide complexes include the iron cyanide complexes prevalent in many cyanide containing industrial wastewaters. The iron cyanide complexes are considered to be among the most stable and least toxic forms of cyanide. Refer to Guide D6696 for a more detailed discussion of aqueous cyanide species.

3.2.9.3 *Discussion*—The metal cyanide complexes can form salts with a variety of alkali and transition metal cations. These alkali metal cyanide complex salts are soluble under alkaline conditions (**1-3**).

3.2.10 *free cyanide, n*—the form of cyanide recognized as being bioavailable and toxic.

3.2.10.1 *Discussion*—Free cyanide may be present as either molecular HCN or the anion CN- depending on the pH conditions. Refer to Guide D6696 for a more detailed discussion of aqueous cyanide species.

4. Summary of Test Method

4.1 Dissolved metal cyanide complexes are determined by anion exchange chromatography. For samples containing from 0.2 to 200 mg/L metal cyanides a sample volume of 0.1 mL is injected directly into the ion chromatograph where the metal cyanide analytes are separated by being differentially retained on the anion exchange column (**4**). The concentration range will differ depending on the specific metal cyanide analyte, with some complexes exhibiting greater or lesser detection sensitivity than others based on their molar absorptivity. Refer to 12.2 for actual concentration ranges for individual metal cyanide complexes. The metal cyanide complexes are eluted from the column by the eluent gradient and detected as signal peaks using UV absorption at 215 nm. Their concentrations in the sample are determined by comparison of the analyte peak area with a standard calibration plot. Under the alkaline conditions of the analysis, ferricyanide ($[Fe(CN)_6]^{3-}$) is reduced to ferrocyanide ($[Fe(CN)_6]^{4-}$) (**1, 2**), yielding a single analyte peak. Any unreduced ferricyanide will be exhibited as tailing on the ferrocyanide peak.

4.2 For samples containing from 0.50 to 200 µg/L, dissolved metal cyanide complexes are determined by using anion exchange chromatography coupled with on-line sample preconcentration (**4, 5**). Twenty mL of sample is passed through an anion exchange concentrator column. As the sample passes through the column, the metal cyanide complexes are retained and concentrated on the column while the remainder of the sample matrix is directed to waste. Following concentration, the metal cyanide analytes are eluted from the concentrator column through gradient elution, into the chromatograph and onto an anion exchange column where the remainder of the analysis is completed as described in 4.1. The calibration range for metal cyanide complexes using sample preconcentration method is between 0.50 to 200 µg/L. This range will differ depending on the specific metal cyanide analyte, with some complexes exhibiting greater or lesser detection sensitivity than others based on their molar absorptivity. Refer to 12.2 for actual concentration ranges for individual metal cyanide complexes.

5. Significance and Use

5.1 This method directly determines the concentration of metal cyanide complexes in environmental waters. The method is important from an environmental regulatory perspective because it differentiates metal cyanide complexes of lesser toxicity from metal cyanide complexes of greater toxicity. Previous determinations of strong metal cyanide complexes

assumed that the concentration of strong metal cyanide complexes is equivalent to the difference between the total cyanide and the free cyanide. This approach is subject to error because different methods used to determine free cyanide often provide widely varying results, thus impacting the strong metal cyanide complex concentration that is determined by difference. The direct analysis using anion exchange chromatography avoids these method biases and provides for a more accurate and precise determination of metal cyanide complexes.

6. Interferences

6.1 Photodecomposition of some metal cyanide complexes such as those of iron can reduce their concentration (**6-8**). Samples shall be collected so as to prevent exposure to light (see 10.2). Samples shall be analyzed in amber bottles and protected from light whenever possible.

6.2 Carbonate is not a method interference but can accumulate by adherence to the anion exchange resin of the analytical column. This may eventually lead to unstable baselines and a reduction in column capacity and analyte retention. Care shall be taken to avoid carbonate contamination when preparing and using sodium hydroxide eluents (**9, 10**). (**Warning—** Carbonate is formed in sodium hydroxide solutions by reaction with atmospheric carbon dioxide. Prepare all eluents using reagent water degassed by helium sparging or vacuum sonication to prevent carbonate contamination as well as eluent outgassing during the analysis. Guidelines are provided in the test method for preparing low-carbonate sodium hydroxide eluent and reagent solutions (see Refs **9, 10**).)

6.3 Commercial grade sodium cyanide used in the preparation of Eluent 1 (see 8.12) often contains metal cyanide complex impurities. These impurities can cause noisy, unstable baselines during the gradient elution profile. The installation of an anion trap column between the Eluent 1 reservoir and the gradient pump removes the impurities from the eluent stream resulting in improved chromatographic baselines. Guidelines for preparing and installing the anion trap column are provided in the test method (see 7.1.6 and 11.6).

6.4 The IonPac[4] AG5, AG11, AS5 and AS11 chromatography columns referenced in the test method (see 7.1.7, 7.1.8, and 7.2.4) are polymeric and accordingly will concentrate neutral organics and polyvalent organic anions at the head of the column. Organic species containing a carbonate functional group will absorb at 215 nm. These species can potentially cause "ghost" peaks when eluted during the analysis. This effect is a function of the quality of the water used in the preparation of the eluent solutions as well as the column equilibration time. Sample preconcentration will enhance this effect. High purity reagent water containing as low a concentration as possible of organic contaminants should be used in the preparation of reagents (see 8.2).

6.5 Free metal cations present in either the sample matrix or as impurities in the combined eluent stream can combine with the free cyanide present in Eluent 1 (see 8.12) to form extraneous metal cyanide complexes. Metal free trap columns should be installed to prevent positive interference by extraneous metal cyanide complexes during the low-level analysis procedure (see 7.2.5).

6.6 The method calibration for iron cyanide is based on its reduced form, ferrocyanide. Although the alkaline conditions of the analysis favor the reduction of ferricyanide to ferrocyanide, any unreduced species could potentially contribute to a bias in the analytical results.

6.7 Matrices with relatively high ionic strength or high total dissolved solids, for example, ocean water, will affect the performance of the analytical columns, resulting in poor separation and recovery of the metal cyanide complexes.

6.8 When performing anion exchange chromatography coupled with on-line sample preconcentration, the silver and copper cyanide complexes exhibit reduced precision and increased bias, especially in high ionic strength matrices, for example, certain wastewaters. For the silver cyanide complex, large front-end tailing in samples containing high total dissolved solids affects peak resolution. For the copper and silver cyanide complexes possible dissociation during the analysis might also affect quantitation in samples containing high total dissolved solids. Any matrix with high ionic strength and total dissolved solids (TDS > 1000 mg/L) could affect the performance of the analytical columns when performing sample preconcentration, which may result in poor separation and recovery of metal cyanide complexes.

7. Apparatus

7.1 *Anion Exchange Chromatography Apparatus Requirements:*

7.1.1 *Pressurized Eluent Reservoir*—Accessories must include a gas regulator capable of maintaining a 13.8 to 68.9 kPa (2 to 10 psi) head pressure on the eluent solutions using helium gas.

7.1.2 *Pressurizable Eluent Bottles*—Bottles must be capable of withstanding an internal pressure of 51 to 68.9 kPa (7 to 10 psi). The bottles must be made of a chemically inert plastic such as polypropylene, suitable for use with sodium hydroxide-based eluents.

7.1.3 *Tubing*—To be used with the eluent reservoir and made of a material that is compatible with the eluent solutions.

7.1.4 *Gradient Pump*—High performance liquid chromatography (HPLC) or ion chromatography (IC) pump capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 1379 to 13790 kPa (200 to 2000 psi).

7.1.5 *Chromatography Tubing*—The tubing must be pressure resistant (approximately 20682 kPa {3000 psi}) and made of a material that is compatible with the eluent solutions. Examples of suitable materials are polyether ether ketone (PEEK) and 316 stainless steel.

7.1.6 *Anion Trap Column*—The anion trap column is a low pressure column that is placed between the Eluent 1 reservoir and the gradient pump inlet to trap and remove metal cyanide impurities. The column is packed with a high-capacity anion exchange resin. An example of a suitable column is the Dionex IonPac ATC-3 4-mm (9 by 24 mm) or equivalent (**11**). The

[4] A trademark by Dionex Corporation, Sunnyvale, CA.

column must be composed of a material appropriate for use with sodium hydroxide eluents.

7.1.7 *Analytical Column*—Low-capacity anion exchange chromatography column. The selected column must provide for adequate selectivity of highly valent metal cyanide complexes. Examples include the Dionex IonPac AS5 (4-mm) and the Dionex IonPac AS11 (4-mm or 2-mm) columns, or equivalent (**9, 10**). These columns differ somewhat in selectivity. The AS5 column provides greater selectivity for the early eluting silver, copper and gold cyanide complexes while the AS11 column provides greater selectivity for the iron cyanide complex. The 2-mm column requires ¼ the sample volume and operates at ¼ the flowrate of a 4-mm column. Due to the decreased flowrate, the 2-mm column consumes only ¼ the eluent required by a 4-mm column.

7.1.8 *Guard Column*—Optional low-capacity anion exchange chromatography guard column. This column may be used before the analytical column to remove sample impurities and prevent them from passing onto the analytical column. The selected column shall provide for adequate selectivity of highly valent metal cyanide complexes. Examples include the Dionex IonPac AG5 and IonPac AG11 columns or equivalent (**9, 10**).

7.1.9 *UV/Vis Detector*—Liquid chromatography UV/Vis detector, capable of low wavelength detection at 215 nm.

7.1.10 *Instrument Control and Data Collection System*—Standard equipment such as electronic control devices and computer and software and/or integrators for providing automatic control of the chromatography system, instrument calibration and data analysis.

7.2 *On-line Sample Preconcentration Accessories*—Additional electrical contact closures are required for establishing automatic control of the preconcentration hardware accessories.

7.2.1 *Injection Valve*—-way switching valve capable of injecting volumes ranging from 0.1 µL to 1 mL.

7.2.2 *Autosampler*—Capable of handling 40 mL sample vials for use in performing sample preconcentration.

7.2.3 *Large Sample Vials*—40 mL amber glass vials. The use of self-sealing vials is recommended to prohibit exposure of the sample to light during and after sample injection so as to prevent photodecomposition of some metal cyanide complexes.

7.2.4 *Concentrator Column*—Low-capacity anion exchange chromatography concentrator column. The selected column shall provide for adequate selectivity of highly valent transition metal cyanide complexes. Examples are the Dionex IonPac AG5 and IonPac AG11 columns or equivalent.

7.2.5 *Metal Free Trap Column (MFC)*—Specially designed column for the on-line cleanup of eluent ionic transition metal impurities. Two such columns should be installed; one between the gradient pump outlet and the injection valve and the other between the sample concentrator pump outlet and the injection valve (see 7.2.1). An example is the Dionex IonPac MFC-1 or equivalent (**12**). Refer to the manufacturer's instructions for column preparation and clean-up.

7.2.6 *Sample Concentrator Pump*—Liquid chromatography or otherwise equivalent pump capable of interfacing with the instrument control and data collection system. The selected sample pump must be capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 1379 to 13790 kPa (200 to 2000 psi).

7.3 *Plastic Volumetric Flasks*—1000 mL and 100 mL.

7.4 *Amber Reagent Bottles*—1000 mL and 100 mL.

7.5 *Membrane Syringe Filters*—25 mm diameter, 0.2 to 0.45 µm pore size, having low background extractables, used to filter sample particulates.

7.6 *Plastic Syringes*—5 and 10 mL volumes.

7.7 *pH Electrode and Meter.*

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals must 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.[5]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. It is recommended that special precautions such as routine contaminant monitoring and/or frequent replacement of polishing cartridges be taken to ensure that the total organic carbon content of the water is ≤ 100 µg/L. This practice will limit the elution of organic species and subsequent appearance of "ghost" peaks in the chromatograms (see 6.4). Figs. 1 and 2 provide examples of blank chromatograms.

8.3 *Degassed Reagent Water*—Sparge reagent water with helium gas or sonicate under vacuum for approximately 20 min to remove dissolved gases such as carbon dioxide.

8.4 *Cobalt Cyanide Solution, Stock (1.00 mL = 1000 µg $[Co(CN)_6]^{3-}$)*—Dissolve exactly 1.5455 g of Potassium hexacyanocobaltate (III) (potassium cobalt cyanide), $K_3[Co(CN)_6]$, with 500 mL of Sodium Hydroxide Solution II (see 8.34) in a 1000 mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II (see 8.34) and store at ambient temperature in a 1 L amber reagent bottle. The solution is relatively stable and may be stored for up to one month.

8.5 *Cobalt Cyanide I Solution, Standard (1.00 mL = 100 µg $[Co(CN)_6]^{3-}$)*—Dilute exactly 10 mL of $[Co(CN)_6]^{3-}$ Stock Solution (see 8.4) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.6 *Cobalt Cyanide II Solution, Standard (1.00 mL = 10 µg $[Co(CN)_6]^{3-}$)*—Dilute exactly 10 mL of $[Co(CN)_6]^{3-}$ Standard Solution I (see 8.5) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

[5] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., 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 *Unites States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

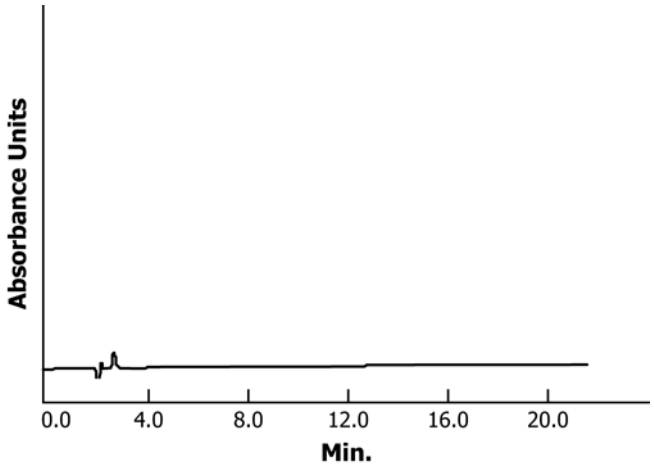


FIG. 1 Blank Chromatogram of Reagent Water

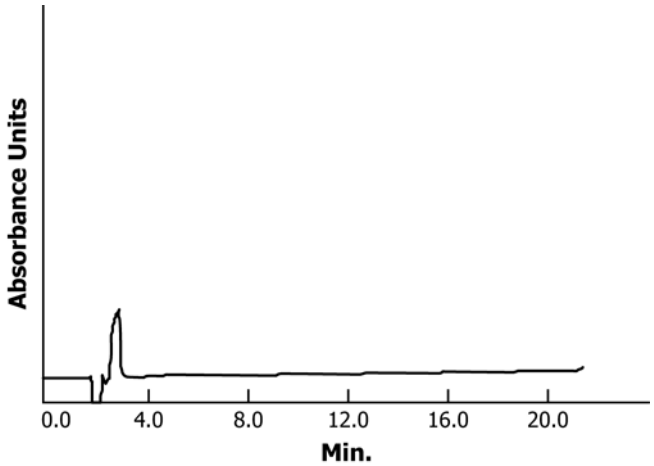


FIG. 2 Blank Chromatogram of Reagent Water Using On-line Sample Preconcentration

8.7 *Cobalt Cyanide III Solution, Standard (1.00 mL = 0.1 µg $[Co(CN)_6]^{3-}$)*—Dilute exactly 1 mL of $[Co(CN)_6]^{3-}$ Standard Solution II (see 8.6) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.8 *Copper Cyanide, Stock (1.00 mL = 1000 µg $Cu[(CN)_3]^{2-}$)*—Combine exactly 0.6325 g of Tricyanocuprate(I) (copper cyanide), CuCN, with 500 mL of Sodium Hydroxide Solution II (see 8.34) in a 1000 mL volumetric flask. Add exactly 1.3844 g of sodium cyanide, NaCN, and stir to dissolve both the copper cyanide and sodium cyanide. Dilute to volume with Sodium Hydroxide Solution II (see 8.34), mix it at least for an hour and store at ambient temperature in a 1 L amber reagent bottle. Prepare daily with analysis. (**Warning—**NaCN is extremely toxic. Avoid inhalation and skin and eye contact (see 9.1.1).) (**Warning—**The copper cyanide will dissolve upon addition of sodium cyanide to form the tricyanocuprate(I) complex, $[Cu(CN)_3]^{2-}$ that is the analyte of interest.)

8.9 *Copper Cyanide I Solution, Standard (1.00 mL = 100 µg $[Cu(CN)_3]^{2-}$)*—Dilute exactly 10 mL of $[Cu(CN)_3]^{2-}$ Stock Solution (see 8.8) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.10 *Copper Cyanide II Solution, Standard (1.00 mL = 10 µg $[Cu(CN)_3]^{2-}$)*—Dilute exactly 10 mL of $[Cu(CN)_3]^{2-}$ Standard Solution I (see 8.9) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.11 *Copper Cyanide III Solution, Standard (1.00 mL = 0.1 µg $[Cu(CN)_3]^{2-}$)*—Dilute exactly 1 mL of $[Cu(CN)_3]^{2-}$ Standard Solution II (see 8.10) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.12 *Eluent 1 (20 mM NaOH, 150 mM NaCN)*—Place 1.6 g of Sodium Hydroxide Solution I (see 8.33) and 7.35 g of sodium cyanide into a plastic 1 L volumetric flask. Add approximately 300 mL of degassed reagent water and swirl to dissolve. Dilute to volume with degassed reagent water and mix thoroughly. The sodium cyanide is used to maintain the integrity of the metal cyanide complexes throughout the analysis.

8.13 *Eluent 2 (20 mM NaOH, 300 mM $NaClO_4 \cdot H_2O$)*—Place 1.6 g of Sodium Hydroxide Solution I (see 8.33) and 42.1 g of sodium perchlorate monohydrate into a plastic 1 L volumetric flask. Add approximately 300 mL of degassed

reagent water and swirl to dissolve. Dilute to volume with degassed reagent water and mix thoroughly. The sodium perchlorate is used to elute the metal cyanide complexes from the analytical column during the gradient elution.

8.14 *Eluent 3 (20 mM NaOH)*—Place 1.6 g of Sodium Hydroxide Solution I (see 8.33) into a plastic 1 L volumetric flask. Dilute to volume with degassed reagent water and mix thoroughly.

8.15 *Gold Cyanide Solution, Stock (1.00 mL = 1000 mg $[Au(CN)_2]^-$)*—Dissolve exactly 1.1570 g of Potassium dicyanoaurate(I) (potassium gold cyanide), $KAu(CN)_2$, with 500 mL of Sodium Hydroxide Solution II (see 8.34) in a 1000 mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II (see 8.34) and store at ambient temperature in a 1 L amber reagent bottle. The solution is relatively stable and may be stored for up to one month.

8.16 *Gold Cyanide I Solution, Standard (1.00 mL = 100 µg $[Au(CN)_2]^-$)*—Dilute exactly 10 mL of $[Au(CN)_2]^-$ Stock Solution (see 8.15) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.17 *Gold Cyanide II Solution, Standard (1.00 mL = 10 µg $[Au(CN)_2]^-$)*—Dilute exactly 10 mL of $[Au(CN)_2]^-$ Standard Solution I (see 8.16) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.18 *Gold Cyanide III Solution, Standard (1.00 mL = 0.1 µg $[Au(CN)_2]^-$)*—Dilute exactly 1 mL of $[Au(CN)_2]^-$ Standard Solution II (see 8.17) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.19 *Helium Gas*—Ultra high purity.

8.20 *Iron Cyanide Solution, Stock (1.00 mL = 1000 µg $[Fe(CN)_6]^{4-}$)*—Dissolve exactly 1.9929 g of Potassium hexacyanoferrate(III) (ferrocyanide trihydrate), $K_4[Fe(CN)_6]\cdot 3H_2O$, with 500 mL of Sodium Hydroxide Solution II (see 8.34) in a 1000 mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II (see 8.34) and store at ambient temperature in a 1 L amber reagent bottle. The solution is relatively stable and may be stored for up to one month.

8.21 *Iron Cyanide I Solution, Standard (1.00 mL = 100 µg $[Fe(CN)_6]^{4-}$)*—Dilute exactly 10 mL of $[Fe(CN)_6]^{4-}$ Stock Solution (see 8.20) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.22 *Iron Cyanide II Solution, Standard (1.00 mL = 10 µg $[Fe(CN)_6]^{4-}$)*—Dilute exactly 10 mL of $[Fe(CN)_6]^{4-}$ Standard Solution I (see 8.21) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.23 *Iron Cyanide III Solution, Standard (1.00 mL = 0.1 µg $[Fe(CN)_6]^{4-}$)*—Dilute exactly 1 mL of $[Fe(CN)_6]^{4-}$ Standard Solution II (see 8.22) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.24 *Nickel Cyanide Solution, Stock (1.00 mL = 1000 µg $[Ni(CN)_4]^{2-}$)*—Dissolve exactly (1.4806 + 0.1107 × *n*) g of Potassium tetracyanonickelate(II) (potassium nickel cyanide) mono- or polyhydrate, $K_2[Ni(CN)_4]\cdot n$H2O (where, *n* = number of water molecules of hydration), with 500 mL of Sodium Hydroxide Solution II (see 8.34) in a 1000 mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II (see 8.34) and store at ambient temperature in a 1 L amber reagent bottle. Prepare daily with analysis.

8.25 *Nickel Cyanide I Solution, Standard (1.00 mL = 100 µg $[Ni(CN)_4]^{2-}$)*—Dilute exactly 10 mL of $[Ni(CN)_4]^{2-}$ Stock Solution (see 8.24) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.26 *Nickel Cyanide II Solution, Standard (1.00 mL = 10 µg $[Ni(CN)_4]^{2-}$)*—Dilute exactly 10 mL of $[Ni(CN)_4]^{2-}$ Standard Solution I (see 8.25) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.27 *Nickel Cyanide III Solution, Standard (1.00 mL = 0.1 µg $[Ni(CN)_4]^{2-}$)*—Dilute exactly 1 mL of $[Ni(CN)_4]^{2-}$ Standard Solution II (see 8.26) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.28 *Reagent Blank*—Use Sodium Hydroxide Solution II (see 8.34).

8.29 *Silver Cyanide Solution, Stock (1.00 mL = 1000 µg $[Ag(CN)_2]^-$)*—Dissolve exactly 1.2445 g of potassium dicyanoargentate(I) (potassium silver cyanide), $K[Ag(CN)_2]$, with 500 mL of Sodium Hydroxide Solution II (see 8.34) in a 1000 mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II (see 8.34) and store at ambient temperature in a 1 L amber reagent bottle. Prepare daily with analysis.

8.30 *Silver Cyanide I Solution, Standard (1.00 mL = 100 µg $[Ag(CN)_2]^-$)*—Dilute exactly 10 mL of $[Ag(CN)_2]^-$ Stock Solution (see 8.29) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.31 *Silver Cyanide II Solution, Standard (1.00 mL = 10 µg $[Ag(CN)_2]^-$)*—Dilute exactly 10 mL of $[Ag(CN)_2]^-$ Standard Solution I (see 8.30) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.32 *Silver Cyanide III Solution, Standard (1.00 mL = 0.1 µg $[Ag(CN)_2]^-$)*—Dilute exactly 1 mL of $[Ag(CN)_2]^-$ Standard Solution II (see 8.31) to 100 mL with Sodium Hydroxide Solution II (see 8.34). Store the solution in an amber reagent bottle. Prepare daily with analysis.

8.33 *Sodium Hydroxide Solution I (50 % w/w)*—It is recommended that the solution be purchased from a vendor so as to have the lowest possible carbonate contamination. Attempts to prepare the solution manually may result in carbonate

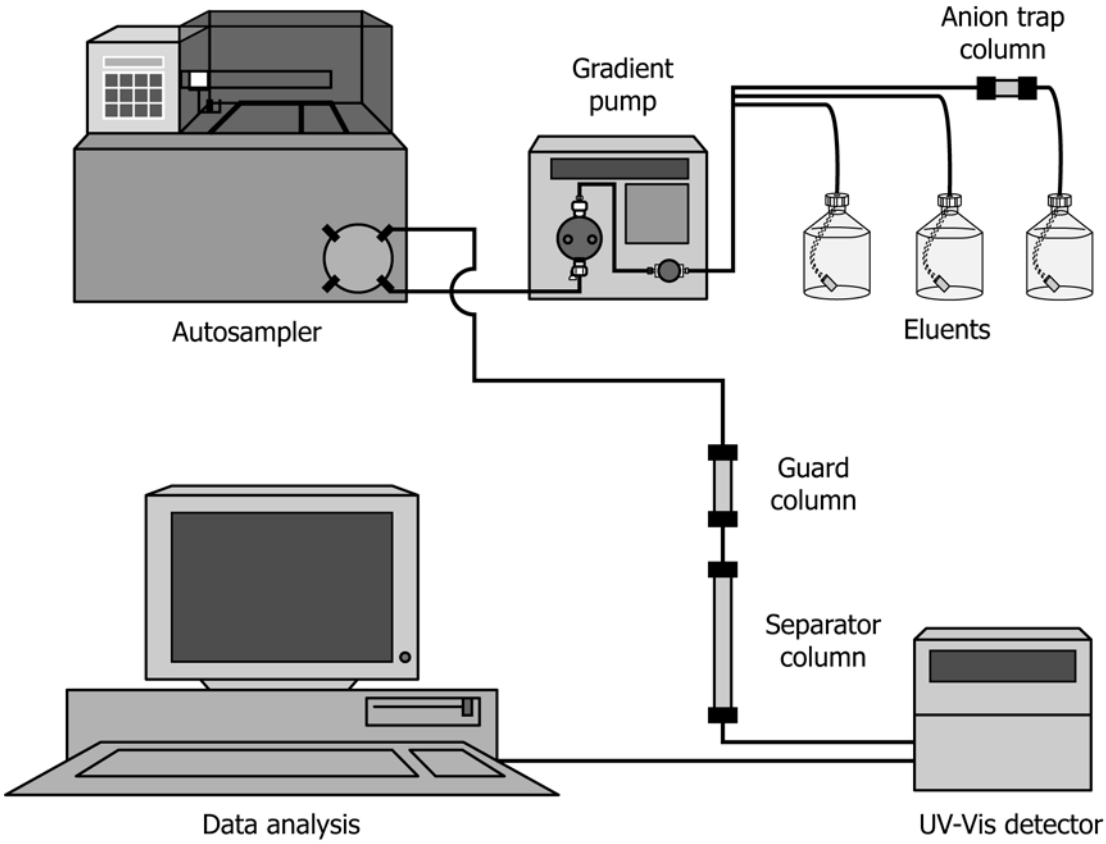


FIG. 3 Chromatograph Configuration for the Analysis of Metal Cyanides

contamination. (**Warning—**This solution is only used for the preparation of reagents and is not a reagent itself.)

8.34 *Sodium Hydroxide Solution II (10 mM, pH = 12)*—Place 0.8 g of Sodium Hydroxide Solution I (see 8.33) into a plastic 1 L volumetric flask. Dilute to volume with degassed reagent water and mix thoroughly. Check to ensure that the pH is ≥ 12 using pH paper or a calibrated pH electrode. Add additional Sodium Hydroxide Solution I, if needed, to bring the pH to 12. This solution is used in the preparation of all standards in order to match the matrix of the standards to that of the alkaline preserved samples. In addition, the high pH acts as a safety measure to prevent formation of gaseous HCN in the event of decomposition of the metal cyanide complex standards.

8.35 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Hazards

9.1 *Safety Precautions:*

9.1.1 Because of the toxicity of cyanide, exercise great care in its handling. Acidification of cyanide solutions produces lethal, toxic hydrogen cyanide (HCN) gas. Prepare all cyanide containing solutions within a ventilation hood. Wear hand and eye protection at all times when working with cyanide.

9.1.2 Some of the reagents and solutions used in this method contain cyanide. Dispose of these materials properly. The effluent from the chromatograph will contain cyanide. The effluent shall be collected and immediately adjusted to a pH of 12 or greater. Dispose of the effluent properly.

10. Sampling and Sample Preservation

10.1 Collect the sample in accordance with Practices D3370.

10.2 Samples must be collected in polyethylene containers covered in aluminum foil or otherwise equivalent containers such as those composed of amber plastic so as to filter UV light at 300 nm and below and prevent photodecomposition of iron and cobalt cyanide complexes.

10.3 Samples for metal cyanide complex analysis must be preserved under alkaline conditions by adjusting the pH to 12 or greater using sodium hydroxide.

10.4 Store samples at 4°C for no longer than 14 days. Samples shall be brought to room temperature prior to analysis.

11. Preparation of Apparatus

11.1 *Anion Exchange Chromatography Analysis*—Analyze samples containing greater than 0.20 mg/L metal cyanide complexes by direct injection of 0.1 mL of sample.

11.1.1 Set up the chromatography hardware in an appropriate manner for analysis. An example of a suitable hardware configuration using the method is displayed in Fig. 3.

TABLE 1 Method Settings for the Analysis of Metal Cyanides Using Gradient Elution

Time	Gradient Pump				Absorbance Detector		Comments and Function
	Flow Rate (mL/min)	Eluent 1 (%)	Eluent 2 (%)	Eluent 3 (%)	Wavelength (nm)	Data Collection (Absorbance Units)	
Init.	1.00	10	10	80	215		Initial Conditions
0.0	1.00	10	10	80	215	Offset baseline	Analysis Gradient
18.0	1.00	10	45	45	215	Begin	
22.0	1.00	10	45	45	215	End	
25.0[A]	1.00	10	10	80	215		Equilibration
35.0	1.00	10	10	80	215		

[A] The eluents are reset to their initial concentrations and allowed to pump for 10 min at the end of the analysis run to equilibrate the columns prior to the next sample injection.

11.2 Set up the method by programming the instrument control and data collection system or the gradient pump directly to perform gradient elution anion chromatography analysis of metal cyanide complexes as specified in Table 1. Portions of the analysis program, such as the gradient elution conditions, may be modified as appropriate provided the analytical results fall within the precision and bias established for the test method (see Section 15).

11.3 *Anion Exchange Chromatography Analysis Using On-line Sample Preconcentration*—Analyze samples containing less than 0.20 mg/L metal cyanide complexes by using on-line sample preconcentration prior to anion exchange chromatography analysis.

11.3.1 Set up the chromatography hardware for performing analysis with initial on-line sample preconcentration. An example of a suitable hardware configuration using the method is displayed in Figs. 4 and 5.

11.3.2 Condition the MFCs per the manufacturer's instructions and install as shown in Fig. 4.

11.3.3 Set the sample concentrator pump for a flow rate of 2 mL/min.

11.3.4 Prime the sample concentrator pump to remove trapped air. Disconnect the tubing from the pump head and withdraw eluent using a plastic syringe until no air bubbles are observed. Reconnect the tubing when finished. (**Warning—** The effluent from the chromatograph will contain cyanide and should be handled and disposed of properly. See 9.1.2.)

11.4 Prime the gradient pump to remove trapped air within each eluent line separately. Select one eluent, set to 100 %, and begin priming. Repeat this step for the remaining eluents.

11.5 Prime the gradient pump once more using the initial method settings.

11.6 Condition the anion trap column according to the manufacturer's instructions.

11.6.1 Connect the anion trap column directly to the outlet of the gradient pump. Set the pump to 100 % Eluent 1 (see 8.12) and pump this through the column at 1 mL/min for 60 min to convert the resin from the hydroxide to the cyanide form. At the end of the time period, stop the gradient pump and disconnect the anion trap column from the outlet of the gradient pump. Dispose of the contents of the waste beaker as hazardous waste.

11.6.2 Place the conditioned anion trap column between the Eluent 1 reservoir and the gradient pump inlet as shown in Figs. 3 and 4. (**Warning—**The anion trap column is capable of treating only a limited amount of Eluent 1. For optimum performance, the column must be reconditioned at a minimum following treatment of each 2 to 3 L of Eluent 1.)

11.7 Reprime the Eluent 1 gradient pump line.

11.8 Connect the guard and analytical columns between the injection valve and the inlet of the UV/Vis detector. Ensure that the columns are oriented in the appropriate direction for eluent flow.

11.9 Allow the instrument to equilibrate for at least 10 min prior to the analysis by pumping eluent through the concentrator column (if present), guard and analytical columns at a flow rate of 1 mL/min using the initial eluent settings.

11.10 Set the UV/Vis detector to 215 nm and offset the absorbance to zero. (**Warning—**Eluent is pumped through the concentrator column by placing the injection valve in the "Inject" mode (see Fig. 5).)

12. Calibration

12.1 (**Warning—**Since all iron cyanide complexes are detected as ferrocyanide ($[Fe(CN)_6]^{4-}$), this form of iron cyanide is used in the preparation of the calibration standards.)

12.2 Prepare calibration standards so as to bracket the calibration ranges of each of the metal cyanide complexes by adding measured volumes of the metal cyanide standards (see Section 8) to volumetric flasks. Approximate calibration ranges for each metal cyanide complex are provided in Tables 3 and 4. Dilute the standards to their respective final volumes using Sodium Hydroxide Solution II (see 8.34). Prepare at least three standards or as otherwise required for regulatory reporting. Store the standards in amber reagent bottles.

12.3 To establish the calibration curves, analyze the reagent blank and calibration standards in accordance with the procedure in Section 13. Plot calibration curves of peak area response versus analyte concentration for each metal cyanide using the reagent blank peak area integration for the zero point. Perform regressions of the plots. The correlation coefficient of each regression should be 0.995 or greater for accurate results. A second order regression plot may be used if needed. Once the calibration curve has been established, verification must be performed on each analysis day, whenever fresh eluent is prepared and once per analysis batch as outlined in 16.3 and 16.4. (**Warning—**The calibration and subsequent analysis results for iron cyanide should be presented as either

TABLE 2 Method Settings for the Analysis of Metal Cyanides Using Gradient Elution and On-line Sample Preconcentration

Time	Two-way Switching Valve Position	Gradient Pump				Absorbance Detector		Sample Enrichment Pump (2 mL/min)	Comments and Function
		Flow Rate (mL/min)	Eluent 1 (%)	Eluent 2 (%)	Eluent 3 (%)	Wavelength (nm)	Data Collection (Absorbance Units)		
Init.	Load	1.00	10	10	80	215			Initial Conditions
0.0	Load	1.00	10	10	80	215			
1.0[A]	Load	1.00	10	10	80	215		On	Equilibration
11.0	Inject	1.00	10	10	80	215		Off	Sample Injection
11.1	Inject	1.00	10	10	80	215	Offset baseline		Analysis Gradient
11.2	Inject	1.00	10	10	80	215	Begin		
29.2	Inject	1.00	10	45	45	215			
33.2	Load	1.00	10	45	45	215	End		

[A] The eluents are pumped through the guard and analytical columns at their initial concentrations for 10 min at the beginning of the analysis run to equilibrate the columns between sample injections. During this time, the sample concentrator pump is turned on and 20 mL of sample is pumped to the concentrator column.

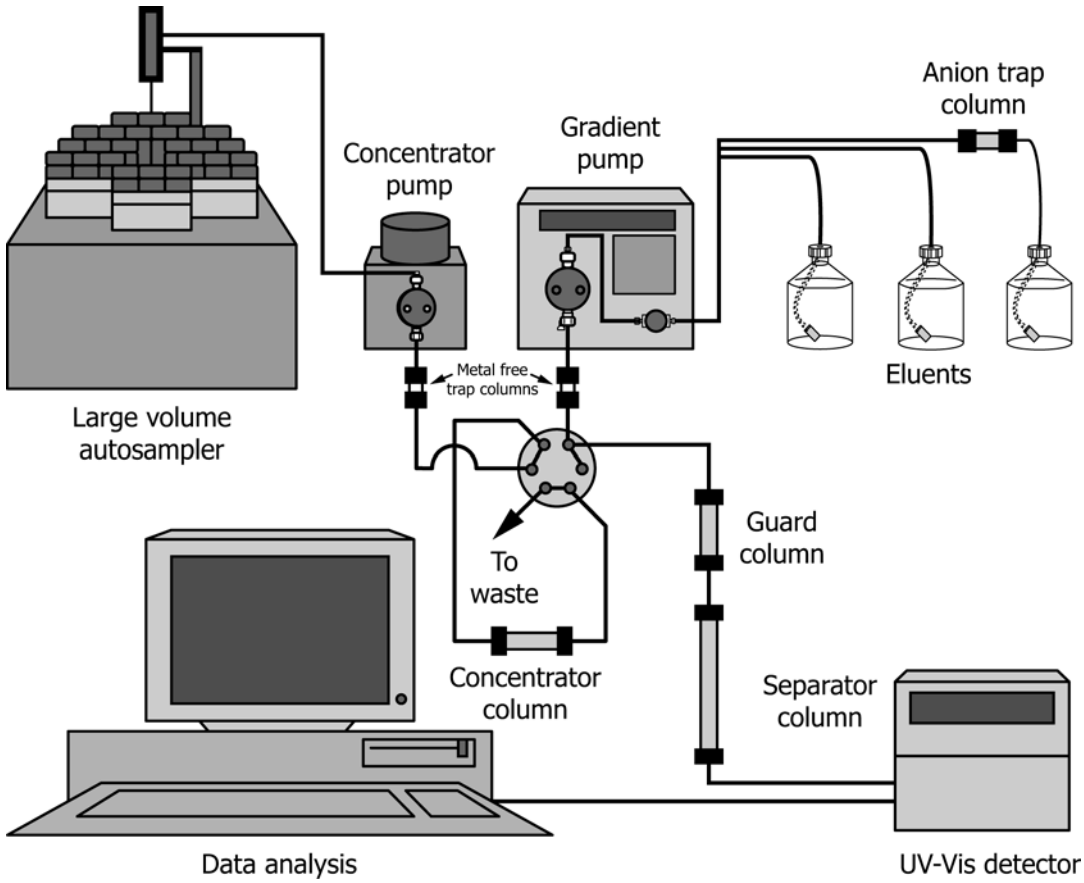


FIG. 4 Chromatograph Configuration for the Analysis of Metal Cyanides Using Sample Preconcentration

$[Fe(CN)_6]^{x-}$ or $[Fe(CN)_6]^{3-/4-}$ so as to represent the total sum of ferrocyanide and ferricyanide.)

13. Procedure

13.1 Filter an appropriate volume of sample using a plastic syringe fitted with a 0.45 µm syringe filter (8.35).

13.2 Transfer the filtered sample to an amber sample vial. Repeat this procedure for the remaining samples.

13.3 Transfer the reagent blank, calibration standards and QA/QC samples (see Section 16) and standards to amber sample vials.

13.4 Place all of the vials in the autosampler.

13.5 Start the autosampler and instrument control and data collection system, if applicable, and begin analyzing the samples. A water blank should be analyzed first to equilibrate the columns followed by the reagent blank, calibration standards (see Section 12) and samples, including QA/QC samples (see Section 16). Use an injection volume of 0.1 mL for samples containing from 0.200 to 200 mg/L metal cyanides and an injection volume of 20 mL when using sample preconcentration for samples containing from 0.50 to 200 µg/L. metal cyanides. Periodically analyze a continuing calibration verification standard to assess instrument drift throughout the run (see 16.3 and 16.4). Examples of method chromatograms are provided in Figs. 6-9.

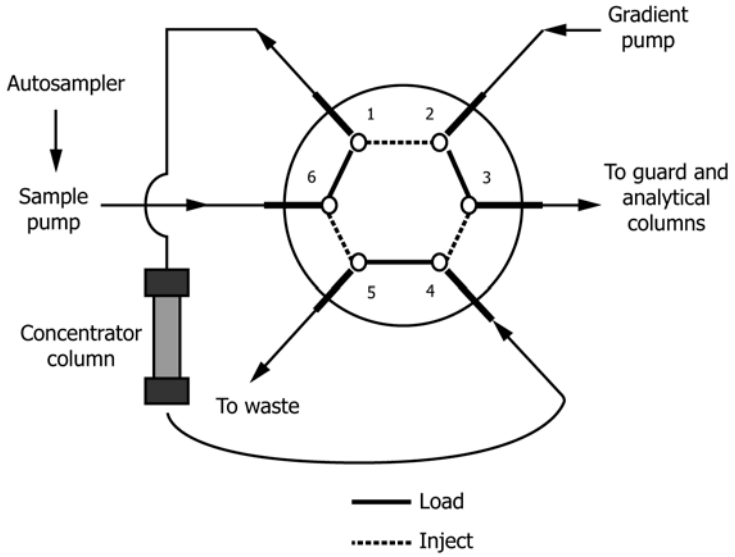


FIG. 5 Injection Valve Configuration for Sample Preconcentration

TABLE 3 Approximate Calibration Ranges for Metal Cyanide Complexes Determined by Anion Exchange Chromatography

Cyanide Complex	Calibration Range (mg/L)
$[Ag(CN)_2]^-$	0.5 to 100
$[Au(CN)_2]^-$	0.2 to 50
$[Co(CN)_6]^{3-}$	0.5 to 100
$[Cu(CN)_3]^{2-}$	0.2 to 2.0
$[Fe(CN)_6]^{4-}$	0.10 to 20
$[Ni(CN)_4]^{2-}$	1.0 to 200

TABLE 4 Approximate Calibration Ranges for Metal Cyanide Complexes Determined by Anion Exchange Chromatography Using On-line Sample Preconcentration

Cyanide Complex	Calibration Range (µg/L)
$[Ag(CN)_2]^-$	10 to 120
$[Au(CN)_2]^-$	5 to 100
$[Co(CN)_6]^{3-}$	1.0 to 200
$[Cu(CN)_3]^{2-}$	1.0 to 5.0
$[Fe(CN)_6]^{4-}$	0.5 to 20
$[Ni(CN)_4]^{2-}$	50 to 100

14. Calculation

14.1 Derive the concentration of each respective metal cyanide analyte in either mg/L or µg/L in the samples using the regression plot from 12.3. Make the necessary adjustments to the final results based on any dilutions that were performed using the following calculation:

$$\frac{\text{µg or mg}}{\text{L}}\left[M(CN)_b\right]^{x-} = \tag{2}$$

$$\frac{\text{µg or mg}}{\text{L}}\left[M(CN)_b\right]^{x-} \text{ in diluted sample} \times \frac{\text{mL final dilution volume}}{\text{mL as received sample}}$$

where:

M = transition metal cation,
b = number of cyanide groups, and
x = ionic charge of the transition metal complex.

14.2 Convert the metal cyanide results to cyanide when reporting the results "as cyanide" based on the following calculation:

$$\frac{\text{µg or mg}}{\text{L}}\left[M(CN)_b\right]^{x-} \text{ as } CN^- = \tag{3}$$

$$\frac{\text{µg or mg}}{\text{L}}\left[M(CN)_b\right]^{x-} \times (b) \times \frac{(\text{Formula Wt. of } CN^-)}{(\text{Formula Wt. of } \left[M(CN)_b\right]^{x-})}$$

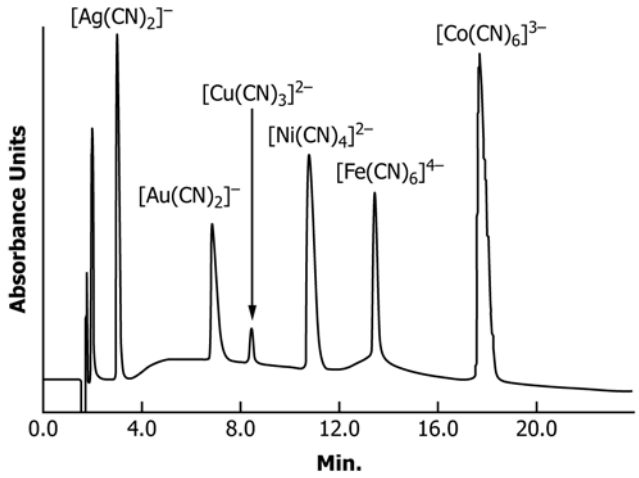
The formula weights for cyanide as well as those for each of the metal cyanide complexes are provided in Table 5.

15. Precision and Bias[6]

15.1 The precision and bias for this test method conforms to Practice D2777 – 98, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

15.2 The interlaboratory study that generated the precision and bias data in this test method for analysis of both mg/L (ppm-level) metal cyanide complex concentrations (using anion exchange chromatography-UV detection) (see 4.1) and µg/L (ppb-level) metal cyanide complex concentrations (using anion exchange chromatography-UV detection with on-line sample preconcentration) (see 4.2) was performed in reagent water, wastewater, drinking water, surface water and groundwater. The ppm-level analysis was performed by eight laboratories using a single operator at each lab. The ppb-level analysis was performed by seven laboratories using a single operator at each lab. Additionally, a single laboratory performed analysis of µg/L metal cyanide complex concentrations using anion exchange chromatography coupled with ICP-MS detection. Details about the single laboratory anion exchange

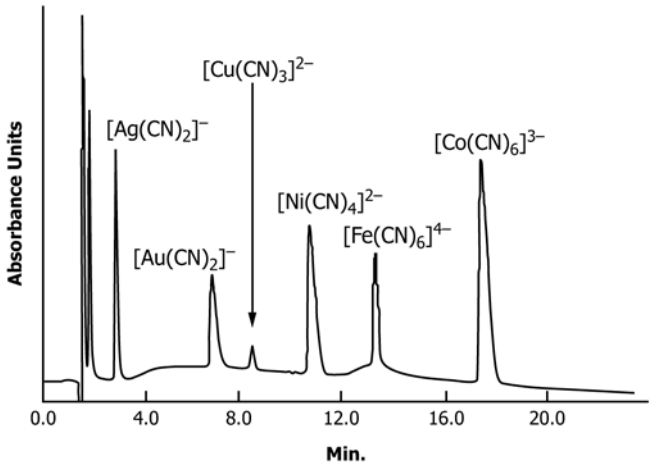
[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1175. Contact ASTM Customer Service at service@astm.org.



Analyte	mg/L
$[Ag(CN)_2]^-$	23
$[Au(CN)_2]^-$	12
$[Cu(CN)_3]^{2-}$	0.24
$[Ni(CN)_4]^{2-}$	24
$[Fe(CN)_6]^{4-}$	1.2
$[Co(CN)_6]^{3-}$	18

Column: Dionex IonPac AG5/AS5

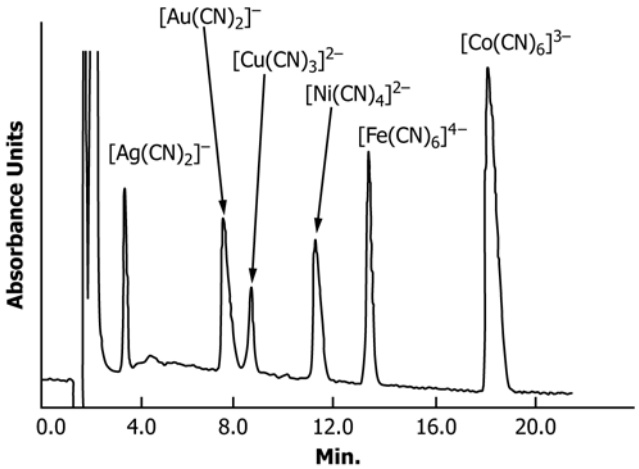
FIG. 6 Reagent Water Chromatogram



Analyte	mg/L
$[Ag(CN)_2]^-$	23
$[Au(CN)_2]^-$	12
$[Cu(CN)_3]^{2-}$	0.24
$[Ni(CN)_4]^{2-}$	24
$[Fe(CN)_6]^{4-}$	1.2
$[Co(CN)_6]^{3-}$	18

Column: Dionex IonPac AG5/AS5

FIG. 7 Groundwater Chromatogram

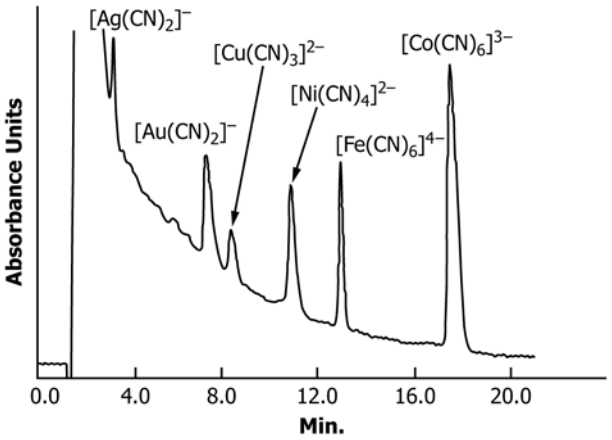


Analyte	µg/L
$[Ag(CN)_2]^-$	100
$[Au(CN)_2]^-$	75
$[Cu(CN)_3]^{2-}$	4
$[Ni(CN)_4]^{2-}$	75
$[Fe(CN)_6]^{4-}$	10
$[Co(CN)_6]^{3-}$	100

Column: Dionex IonPac AG5/AS5

FIG. 8 Reagent Water Chromatogram Using Sample Preconcentration

chromatography-ICP-MS method and precision and bias results are presented in Appendix X1. For each lab, six levels of concentration were used for six analytes, producing three Youden pairs. The Youden pair data was used to calculate the single operator precision (S_o). For each matrix, each laboratory prepared six samples for the precision and bias portion of the ILV study by mixing the entire contents (equivalent to 5 mL) of the six supplied spiking solutions to the six supplied 100 mL sample bottles, each containing 90 mL of preserved matrix. Each spike solution vial was then rinsed with the entire



Analyte	µg/L
$[Ag(CN)_2]^-$	100
$[Au(CN)_2]^-$	75
$[Cu(CN)_3]^{2-}$	4
$[Ni(CN)_4]^{2-}$	75
$[Fe(CN)_6]^{4-}$	10
$[Co(CN)_6]^{3-}$	100

Column: Dionex IonPac AG5/AS5

FIG. 9 Groundwater Chromatogram Using Sample Preconcentration

TABLE 5 Cyanide Species Formula Weights

Cyanide Complex	Formula Weight (mg/mmol)
CN^-	26.0177
$[Ag(CN)_2]^-$	159.903
$[Au(CN)_2]^-$	249.002
$[Co(CN)_6]^{3-}$	215.039
$[Cu(CN)_3]^{2-}$	141.599
$[Fe(CN)_6]^{4-}$	211.953
$[Ni(CN)_4]^{2-}$	162.771

contents (equivalent to 5 mL) of rinse solution and the solution was poured in each sample bottle. This resulted in a 20-fold dilution of the spike solutions. Each sample bottle was then shaken gently to mix.

15.2.1 A quality control (QC) sample was supplied (as a concentrate) to serve as initial, and on-going, calibration verification. A separate method detection limit (MDL) sample was supplied (as a concentrate) for the determination of the pooled MDL values. The QC sample for the ppm-level study was prepared by pipetting a 5.0 mL aliquot of the QC concentrate into a clean volumetric flask; adding 1.0 g of NaOH, and diluting to a total of 250 mL with reagent water. The QC sample for the for the ppb-level study was prepared by pipetting a 1.0 mL aliquot of the QC concentrate into a clean volumetric flask; adding 1.0 g of NaOH, and diluting to a total of 500 mL with reagent water. The MDL sample for the ppm-level study was prepared by pipetting a 1.0 mL aliquot of the MDL concentrate into a clean volumetric flask; adding 1.0 g of NaOH, and diluting to a total of 100 mL with reagent water. The MDL sample for the ppb-level study was prepared by pipetting a 2.0 mL aliquot of the MDL concentrate into a clean volumetric flask; adding 1.0 g of NaOH, and diluting to a total of 200 mL with reagent water.

15.3 The precision and bias of the ppm-level study for each of the six metal cyanide complexes for reagent water, wastewater, surface water, groundwater and drinking water are shown in Tables 6-11.

15.4 The precision and bias of the ppb-level study for each of the six metal cyanide complexes for reagent water, wastewater, surface water, groundwaters and drinking water are shown in Tables 12-17.

15.5 The results of the ppm-level interlaboratory study can also be summarized as regression equations, as shown in Tables 18-22 for reagent water, wastewater, surface water, groundwater and drinking water.

15.6 The results of the ppb-level interlaboratory study can also be summarized as regression equations, as shown in Tables 23-28 for reagent water, wastewater, surface water, groundwaters and drinking water.

15.7 In addition to performing the analyses required to generate the precision and bias data shown in Tables 6-16, the participating laboratories each analyzed seven replicates of an MDL sample using both the ppm-level (anion exchange chromatography-UV detection) and ppb-level (anion exchange chromatography-UV detection with on-line sample preconcentration) methods. The MDLs were derived for each laboratory using the students *t*-test at six degrees of freedom, as follows:

$$MDL = (t) \times (S) \quad (4)$$

where:

t = students t value for a 99 % confidence level and a standard deviation estimate with n^{-1} degrees of freedom [t = 3.14 for seven replicates], and

S = standard deviation of the replicate analysis.[7]

The true amounts injected, mean value determined, and pooled MDL values are shown for the ppm-level and ppb-level methods in Tables 29 and 30.

16. Quality Control

16.1 Before this test method is applied to the analysis of samples of unknown cyanide concentration, the analyst must establish quality control by the procedures recommended in Practice D5847 and Guide D3856.

16.2 The laboratory using this test should perform an initial demonstration of laboratory capability. Analyze seven replicates of an Initial Demonstration of Performance (IDP) solution. The IDP solution is a solution of reagent water adjusted with sodium hydroxide solution to pH 12 or greater and fortified with method analytes at known concentrations and

[7] Code of Federal Regulations 40, Ch. 1., Pt. 136, Appendix B.

TABLE 6 Determination of Precision and Bias
Analyte: $[Fe(CN)_6]^{4-}$

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (mg/L)	S_t (mg/L)	Bias
Reagent Water	1	1.08	7			0.06	8.4%
	1.2	1.30	6	6	0.03	0.03	8.2%
	9	9.48	6			0.10	5.3%
	10	10.49	7	6	0.14	0.31	4.9%
	17.5	18.45	6			0.28	5.4%
	18.5	19.30	7	6	0.24	0.57	4.3%
Wastewater	1	0.98	6			0.02	-1.5%
	1.2	1.22	7	6	0.06	0.10	1.7%
	9	9.17	7			0.30	1.9%
	10	10.21	7	7	0.18	0.44	2.1%
	17.5	17.99	7			1.16	2.8%
	18.5	18.82	7	7	0.41	0.73	1.8%
Surface Water	1	1.06	7			0.05	6.1%
	1.2	1.29	7	7	0.03	0.04	7.5%
	9	9.46	7			0.12	5.2%
	10	10.51	7	7	0.06	0.16	5.1%
	17.5	18.22	7			0.31	4.1%
	18.5	19.33	7	7	0.22	0.48	4.5%
Groundwater	1	1.05	7			0.02	4.7%
	1.2	1.28	7	7	0.02	0.04	6.4%
	9	9.41	6			0.09	4.6%
	10	10.51	7	6	0.07	0.24	5.1%
	17.5	18.29	7			0.42	4.5%
	18.5	19.27	7	7	0.07	0.36	4.2%
Drinking Water	1	1.06	7			0.05	5.9%
	1.2	1.28	7	7	0.02	0.03	7.0%
	9	9.55	6			0.04	6.1%
	10	10.49	7	6	0.04	0.10	4.9%
	17.5	18.38	7			0.25	5.0%
	18.5	19.31	7	7	0.13	0.26	4.4%

TABLE 7 Determination of Precision and Bias
Analyte: $[Cu(CN)_2]^{2-}$

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (mg/L)	S_t (mg/L)	Bias
Reagent Water	0.2	0.22	7			0.02	10.0%
	0.24	0.30	6	6	0.01	0.01	23.9%
	0.9	0.97	6			0.06	7.3%
	1	1.08	7	6	0.03	0.12	8.2%
	1.6	1.81	7			0.15	13.0%
	1.7	1.94	6	6	0.03	0.11	14.2%
Wastewater	0.2	0.08	6			0.05	-60.3%
	0.24	0.13	6	6	0.01	0.05	-44.7%
	0.9	0.79	7			0.07	-12.6%
	1	0.89	6	6	0.07	0.11	-11.5%
	1.6	1.56	7			0.12	-2.5%
	1.7	1.66	7	7	0.04	0.13	-2.3%
Surface Water	0.2	0.24	7			0.05	18.9%
	0.24	0.29	6	6	0.01	0.03	20.0%
	0.9	1.01	7			0.09	12.1%
	1	1.11	7	7	0.02	0.11	10.8%
	1.6	1.80	7			0.09	12.8%
	1.7	1.93	7	7	0.03	0.09	13.6%
Groundwater	0.2	0.22	7			0.01	7.9%
	0.24	0.29	7	7	0.01	0.02	22.7%
	0.9	0.96	6			0.04	6.9%
	1	1.04	7	6	0.02	0.04	4.4%
	1.6	1.74	7			0.11	8.7%
	1.7	1.83	7	7	0.01	0.13	7.6%
Drinking Water	0.2	0.22	6			0.02	11.8%
	0.24	0.33	7	6	0.02	0.07	37.0%
	0.9%	1.00	7			0.13	10.9%
	1	1.05	6	6	0.01	0.06	4.7%
	1.6	1.78	7			0.19	11.1%
	1.7	1.90	7	7	0.09	0.11	11.8%

prepared from a different source than that used to prepare the calibration standards. Ideally, the IDP solution should be

TABLE 8 Determination of Precision and Bias
Analyte: $[Ag(CN)_2]^-$

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (mg/L)	S_t (mg/L)	Bias
Reagent Water	21	22.94	7			1.22	9.2%
	23	25.31	7	7	0.59	1.09	10.1%
	46	50.13	6			1.80	9.0%
	51	55.46	7	6	0.49	1.56	8.7%
	85	88.36	7			1.61	3.9%
	90	94.00	7	7	1.42	1.82	4.4%
Wastewater	21	16.80	7			4.06	-20.0%
	23	18.35	7	7	1.53	5.27	-20.2%
	46	39.62	7			9.30	-13.9%
	51	44.68	7	7	1.04	9.81	-12.4%
	85	73.99	7			19.95	-13.0%
	90	77.27	7	7	1.99	20.96	-14.1%
Surface Water	21	23.27	7			1.31	10.8%
	23	25.47	7	7	0.30	1.14	10.7%
	46	50.08	7			1.61	8.9%
	51	55.55	7	7	0.37	1.73	8.9%
	85	89.10	7			1.91	4.8%
	90	94.68	7	7	1.36	2.18	5.2%
Groundwater	21	23.68	7			0.54	12.8%
	23	25.90	7	7	0.84	0.92	12.6%
	46	50.86	7			1.47	10.6%
	51	55.86	7	7	0.47	1.11	9.5%
	85	90.37	7			2.20	6.3%
	90	94.77	7	7	0.45	2.08	5.3%
Drinking Water	21	23.97	7			1.06	14.1%
	23	26.04	7	7	0.38	0.93	13.2%
	46	51.18	7			1.54	11.3%
	51	55.71	7	7	0.44	1.62	9.2%
	85	90.63	7			1.10	6.6%
	90	94.91	7	7	0.84	1.66	5.4%

TABLE 9 Determination of Precision and Bias
Analyte: $[Au(CN)_2]^-$

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (mg/L)	S_t (mg/L)	Bias
Reagent Water	10	10.98	7			0.64	9.8%
	12	12.59	6	6	0.40	0.26	4.9%
	20	22.00	7			1.97	10.0%
	22	23.09	6	6	1.34	0.58	5.0%
	40	41.57	6			0.86	3.9%
	42	43.29	6	6	0.47	0.93	3.1%
Wastewater	10	9.01	7			1.41	-9.9%
	12	11.01	7	7	0.42	1.04	-8.3%
	20	19.11	7			1.59	-4.5%
	22	21.55	7	7	0.70	2.29	-2.0%
	40	38.41	7			2.68	-4.0%
	42	39.11	7	7	1.63	3.90	-6.9%
Surface Water	10	10.60	7			0.60	6.0%
	12	12.67	7	7	0.30	0.52	5.6%
	20	20.99	7			0.46	4.9%
	22	22.98	7	7	0.30	0.57	4.5%
	40	42.03	6			0.47	5.1%
	42	44.12	6	6	0.51	0.79	5.1%
Groundwater	10	10.53	6			0.41	5.3%
	12	12.38	7	6	0.43	0.69	3.1%
	20	21.56	7			1.13	7.8%
	22	22.73	7	7	1.43	1.26	3.3%
	40	42.27	6			0.83	5.7%
	42	44.00	6	6	0.55	0.81	4.8%
Drinking Water	10	10.38	7			0.52	3.8%
	12	12.33	7	7	0.15	0.40	2.7%
	20	20.89	7			0.58	4.5%
	22	22.84	7	7	0.32	0.65	3.8%
	40	42.51	6			0.89	6.3%
	42	44.30	6	6	0.58	0.49	5.5%

prepared by an independent source from certified reference materials. The mean and standard deviation of the seven values

TABLE 10 Determination of Precision and Bias
Analyte: $[Co(CN)_6]^{3-}$

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (mg/L)	S_t (mg/L)	Bias
Reagent Water	15	15.63	7			0.39	4.2%
	18	18.67	7	7	0.23	0.40	3.7%
	46	47.78	6			0.40	3.9%
	50	51.42	6	6	0.25	0.14	2.8%
	85	86.17	7			0.66	1.4%
	90	91.01	7	7	0.68	1.52	1.1%
Wastewater	15	15.42	7			0.41	2.8%
	18	18.65	7	7	0.23	0.45	3.6%
	46	47.76	7			1.44	3.8%
	50	50.87	7	7	0.70	1.59	1.7%
	85	85.43	7			2.05	0.5%
	90	90.90	7	7	0.89	2.21	1.0%
Surface Water	15	16.11	7			0.55	7.4%
	18	19.25	7	7	0.28	0.48	6.9%
	46	48.67	7			1.16	5.8%
	50	52.46	7	7	0.33	1.05	4.9%
	85	87.56	7			1.51	3.0%
	90	92.97	7	7	0.75	1.92	3.3%
Groundwater	15	15.71	7			0.48	4.7%
	18	18.83	7	7	0.18	0.32	4.6%
	46	47.87	7			0.91	4.1%
	50	51.31	7	7	0.27	1.12	2.6%
	85	86.48	7			1.75	1.7%
	90	91.35	7	7	0.21	1.93	1.5%
Drinking Water	15	16.05	7			0.37	7.0%
	18	19.17	7	7	0.25	0.39	6.5%
	46	48.80	7			0.80	6.1%
	50	52.04	7	7	0.33	0.78	4.1%
	85	87.79	7			1.49	3.3%
	90	92.38	7	7	0.54	1.68	2.6%

TABLE 11 Determination of Precision and Bias
Analyte: $[Ni(CN)_4]^{2-}$

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (mg/L)	S_t (mg/L)	Bias
Reagent Water	20	21.93	7			0.98	9.6%
	24	25.91	7	7	0.48	1.18	7.9%
	85	91.15	7			2.10	7.2%
	95	101.57	7	7	0.72	2.40	6.9%
	175	185.87	7			9.64	6.2%
	185	193.53	7	7	2.33	8.65	4.6%
Wastewater	20	20.98	7			1.45	4.9%
	24	25.34	7	7	0.39	1.36	5.6%
	85	88.22	7			3.70	3.8%
	95	99.50	7	7	1.36	2.39	4.7%
	175	178.41	7			5.40	1.9%
	185	187.74	7	7	2.32	5.86	1.5%
Surface Water	20	21.60	7			1.22	8.0%
	24	25.84	7	7	0.55	1.48	7.6%
	85	90.47	7			1.88	6.4%
	95	100.82	7	7	0.77	2.59	6.1%
	175	181.32	7			3.40	3.6%
	185	191.83	7	7	2.67	3.43	3.7%
Groundwater	20	21.62	7			1.67	8.1%
	24	25.47	7	7	0.43	1.74	6.1%
	85	90.49	6			1.05	6.5%
	95	99.72	7	6	0.75	3.32	5.0%
	175	181.53	7			4.22	3.7%
	185	190.73	7	7	1.58	2.99	3.1%
Drinking Water	20	21.35	7			1.44	6.8%
	24	25.38	7	7	0.39	1.29	5.8%
	85	90.21	7			1.92	6.1%
	95	100.46	7	7	0.76	2.13	5.8%
	175	183.95	7			6.23	5.1%
	185	191.26	7	7	1.23	5.18	3.4%

should then be calculated and compared, according to Practice D5847, to the single operator precision established for this Test

TABLE 12 Determination of Precision and Bias
Analyte: $[Fe(CN)_6]^{4-}$

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (µg/L)	S_t (µg/L)	Bias
Reagent Water	1.6	1.68	6			0.08	5.1%
	1.8	1.87	5	5	0.06	0.02	3.9%
	9.5	9.08	6			0.86	-4.4%
	11	10.90	6	6	0.38	0.41	-1.0%
	17	16.53	6			1.16	-2.8%
	18	17.49	6	6	1.06	0.88	-2.9%
Wastewater	1.6	2.25	6			0.68	40.4%
	1.8	1.78	5	5	0.48	0.64	-1.0%
	9.5	8.42	6			0.63	-11.3%
	11	10.02	6	6	0.28	0.60	-8.9%
	17	14.44	5			1.80	-15.1%
	18	16.45	6	5	1.23	0.60	-8.6%
Surface Water	1.6	1.65	5			0.04	3.3%
	1.8	1.81	5	5	0.10	0.11	0.8%
	9.5	9.38	6			1.37	-1.3%
	11	10.77	5	5	0.41	0.32	-2.1%
	17	17.06	6			2.07	0.4%
	18	18.01	6	6	1.06	1.85	0.0%
Groundwater 1	1.6	1.94	5			0.53	20.9%
	1.8	1.37	5	4	0.66	0.78	-23.7%
	9.5	7.42	6			1.28	-21.9%
	11	7.86	6	6	1.15	2.22	-28.5%
	17	13.39	6			2.81	-21.2%
	18	12.04	6	6	1.57	4.76	-33.1%
Groundwater 2	1.6	2.17	6			0.49	35.4%
	1.8	2.22	5	5	0.28	0.16	23.5%
	9.5	9.72	6			1.60	2.3%
	11	10.94	5	5	0.30	0.50	-0.5%
	17	17.53	5			0.98	3.1%
	18	18.08	5	5	0.92	0.46	0.4%
Drinking Water	1.6	2.45	7			0.80	53.0%
	1.8	2.29	7	7	0.17	0.59	27.1%
	9.5	10.01	7			0.78	5.3%
	11	11.13	7	7	0.54	0.76	1.2%
	17	17.72	7			1.40	4.2%
	18	18.21	7	7	0.96	1.03	1.2%

Method. The limits for acceptable precision and the range of acceptable recoveries are detailed below:

Analyte	IDP Solution Amount (mg/L)	Method S_o (mg/L)	Acceptable IDP Precision, $n = 7$
$[Fe(CN)_6]^{4-}$	10	0.14	≤ 0.26
$[Cu(CN)_3]^{2-}$	1	0.03	≤ 0.05
$[Ag(CN)_2]^-$	50	0.77	≤ 1.42
$[Au(CN)_2]^-$	25	0.74	≤ 1.38
$[Co(CN)_6]^{3-}$	50	0.37	≤ 0.68
$[Ni(CN)_4]^{2-}$	100	1.16	≤ 2.13

Analyte	Method Mean Recovery (mg/L)	Lower Acceptable IDP Recovery (mg/L)	Higher Acceptable IDP Recovery (mg/L)
$[Fe(CN)_6]^{4-}$	10.5	9.77	11.2
$[Cu(CN)_3]^{2-}$	1.12	0.83	1.41
$[Ag(CN)_2]^-$	53.3	48.4	58.2
$[Au(CN)_2]^-$	26.3	24.2	28.3
$[Co(CN)_6]^{3-}$	51.1	49.4	52.8
$[Ni(CN)_4]^{2-}$	106.1	90.7	122

Analyte	IDP Solution Amount (µg/L)	Method S_o (µg/L)	Acceptable IDP Precision, $n = 7$
$[Fe(CN)_6]^{4-}$	10	0.48	≤ 0.91
$[Cu(CN)_3]^{2-}$	2.5	0.33	≤ 0.62
$[Ag(CN)_2]^-$	65	3.95	≤ 7.39
$[Au(CN)_2]^-$	50	1.79	≤ 3.37
$[Co(CN)_6]^{3-}$	100	4.53	≤ 8.30
$[Ni(CN)_4]^{2-}$	75	3.48	≤ 6.64

Analyte	Method Mean Recovery (µg/L)	Lower Acceptable IDP Recovery (µg/L)	Higher Acceptable IDP Recovery (µg/L)
$[Fe(CN)_6]^{4-}$	9.77	8.39	11.1
$[Cu(CN)_3]^{2-}$	2.66	1.94	3.39
$[Ag(CN)_2]^-$	62.9	16.5	109
$[Au(CN)_2]^-$	51.6	44.4	58.8
$[Co(CN)_6]^{3-}$	96.7	83.0	110
$[Ni(CN)_4]^{2-}$	74.3	65.4	83.3

16.3 Prior to the analysis of unknown samples, a Calibration Verification Standard (CVS) should be analyzed to verify the instrument calibration and acceptable instrument performance. This verification should be performed on each analysis day or whenever fresh eluent has been prepared. The CVS is a solution of reagent water adjusted with sodium hydroxide solution to pH 12 or greater and fortified with method analytes at known concentrations, ideally prepared at concentrations that are near the mid-range of the analyte calibration curves. If the determined CVS concentrations are not within ±20 % of the known values, the analyst should reanalyze the CVS. If the values still fall outside acceptable limits, a new calibration is required which must be confirmed by a successful CVS before continuing with the on-going analysis.

16.4 A continuing CVS should be analyzed after every tenth field sample and an end CVS should be analyzed at the end of the sample batch (maximum of 20 samples) to verify the

TABLE 13 Determination of Precision and Bias
Analyte: $[Cu(CN)_3]^{2-}$

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (µg/L)	S_t (µg/L)	Bias
Reagent Water	1.1	1.47	6			0.62	34.0%
	1.3	1.05	5	5	0.45	0.30	-19.5%
	2.3	2.25	6			0.20	-2.0%
	2.5	3.22	6	6	0.25	0.35	28.8%
	4.4	4.38	6			0.32	-0.5%
	4.6	4.81	6	6	0.26	0.35	4.6%
Wastewater	1.1	5.92	6			4.93	438.6%
	1.3	6.20	6	6	0.40	5.25	377.2%
	2.3	6.45	6			5.68	180.3%
	2.5	7.36	6	6	1.12	6.32	194.5%
	4.4	5.90	6			4.78	34.2%
	4.6	7.09	6	6	1.02	6.14	54.2%
Surface Water	1.1	1.58	4			1.85	43.8%
	1.3	6.50	4	3	0.85	8.08	400.1%
	2.3	3.21	4			2.61	39.4%
	2.5	2.61	4	4	0.21	2.37	4.4%
	4.4	3.96	4			3.39	-10.1%
	4.6	3.65	4	4	0.19	3.45	-20.7%
Groundwater 1	1.1	2.40	4			2.61	117.8%
	1.3	1.36	3	3	0.17	0.65	4.7%
	2.3	2.81	5			2.36	22.3%
	2.5	3.80	5	5	1.04	3.63	51.8%
	4.4	5.61	5			9.01	27.6%
	4.6	3.49	5	5	4.56	2.71	-24.2%
Groundwater 2	1.1	0.89	4			0.74	-19.1%
	1.3	0.73	5	4	0.25	0.92	-44.2%
	2.3	0.87	5			0.62	-62.0%
	2.5	0.89	5	5	0.09	0.71	-64.3%
	4.4	1.30	5			0.77	-70.3%
	4.6	1.27	5	5	0.21	0.99	-72.4%
Drinking Water	1.1	2.92	4			1.28	165.5%
	1.3	6.45	4	3	0.32	7.10	396.5%
	2.3	3.16	4			1.76	37.3%
	2.5	5.07	5	4	0.59	2.97	102.8%
	4.4	7.04	4			4.76	59.9%
	4.6	7.36	5	4	1.41	6.30	60.1%

previously established calibrations curves. If the continuing and/or end CVS fall outside of the acceptable limits (±20 %), the analyst should reanalyze the CVS. If the analyte concentration still falls outside acceptable limits (±20 %), that analyte is judged to be out of control, and the source of the problem should be identified before continuing with the on-going analysis. All samples following the last acceptable CVS should be reanalyzed.

16.5 A reagent blank (see 8.29) should be analyzed as part of the initial generation of the calibration curves (see 12.3). A blank should also be analyzed with each sample batch (maximum of 20 samples) to check for contamination introduced by the laboratory or use of the test method.

16.6 One Laboratory Control Sample (LCS) should be analyzed with each sample laboratory-defined batch. The LCS is a solution of the method analytes of known concentration prepared in a matrix that sufficiently challenges the test method. It is recommended, but not required to use a second source, if possible and practical for the LCS. The analyte recoveries for the LCS should fall within the control limits of $x \pm 3S$; where x is the mean recovery and (S) is the standard deviation of the mean recovery established from the interlaboratory precision and bias study data at the IDP levels, as shown below:

Analyte	LCS Amount (mg/L)	Lower Recovery Limit (mg/L)	Higher Recovery Limit (mg/L)
$[Fe(CN)_6]^{4-}$	10	9.80	11.2
$[Cu(CN)_3]^{2-}$	1	0.87	1.37
$[Ag(CN)_2]^{-}$	50	48.8	57.8
$[Au(CN)_2]^{-}$	25	23.6	28.9
$[Co(CN)_6]^{3-}$	50	49.4	52.8
$[Ni(CN)_4]^{2-}$	100	93.2	119

Analyte	LCS Amount (µg/L)	Lower Recovery Limit (µg/L)	Higher Recovery Limit (µg/L)
$[Fe(CN)_6]^{4-}$	10	8.03	11.5
$[Cu(CN)_3]^{2-}$	2.5	1.57	3.76
$[Ag(CN)_2]^{-}$	65	23.8	102
$[Au(CN)_2]^{-}$	50	43.9	59.2
$[Co(CN)_6]^{3-}$	100	80.0	113
$[Ni(CN)_4]^{2-}$	75	62.2	86.4

16.7 One Matrix Spike (MS) should be analyzed with each sample laboratory-defined batch to test method recovery. Spike a portion of a water sample from each batch with known concentrations of the method analytes. The MS should be prepared in accordance with the guidance outlined in Guides D5810 and D3856. The percent recoveries of the spike must fall within limits established from the interlaboratory precision and bias study data for the specific matrix type (assuming a background level of zero) according to Practice D5847, as shown below:

TABLE 14 Determination of Precision and Bias
Analyte: $[Ag(CN)_2]^-$

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (µg/L)	S_t (µg/L)	Bias
Reagent Water	20	25.05	6			8.62	25.2%
	24	28.64	6	6	1.57	8.12	19.3%
	50	49.57	6			10.15	-0.9%
	54	60.33	6	6	6.69	15.66	11.7%
	110	97.02	6			15.20	-11.8%
	115	103.13	6	6	3.57	18.88	-10.3%
Wastewater	20	7.19	5			4.33	-64.0%
	24	8.53	4	4	1.24	3.12	-64.5%
	50	17.94	6			4.88	-64.1%
	54	17.38	5	5	2.13	6.98	-67.8%
	110	26.97	6			12.82	-75.5%
	115	34.30	6	6	10.11	9.19	-70.2%
Surface Water	20	10.35	4			6.09	-48.2%
	24	9.92	4	3	1.26	7.06	-58.7%
	50	25.40	5			1.22	-49.2%
	54	23.67	6	5	4.69	6.71	-56.2%
	110	56.27	6			19.59	-48.8%
	115	54.56	6	6	8.26	15.50	-52.6%
Groundwater 1	20	12.72	4			9.64	-36.4%
	24	10.05	5	4	1.32	10.51	-58.1%
	50	24.97	6			16.09	-50.1%
	54	27.98	5	5	7.21	12.84	-48.2%
	110	42.48	6			17.80	-61.4%
	115	44.68	6	6	6.32	21.05	-61.1%
Groundwater 2	20	10.19	5			1.77	-49.1%
	24	15.45	6	5	1.12	4.38	-35.6%
	50	29.11	6			5.94	-41.8%
	54	31.26	6	6	1.61	5.22	-42.1%
	110	62.93	6			9.50	-42.8%
	115	65.63	6	6	1.70	10.35	-42.9%
Drinking Water	20	17.86	6			5.58	-10.7%
	24	23.85	5	5	0.84	3.36	-0.6%
	50	42.90	6			8.91	-14.2%
	54	47.30	6	6	4.09	3.45	-12.4%
	110	91.71	5			10.13	-16.6%
	115	84.12	6	5	1.64	19.43	-26.9%

Analyte	Reagent Water MS Amount (mg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	15	97.5	112
$[Cu(CN)_3]^{2-}$	0.5	83.7	138
$[Ag(CN)_2]^-$	75	98.2	112
$[Au(CN)_2]^-$	25	94.4	116
$[Co(CN)_6]^{3-}$	75	98.2	105
$[Ni(CN)_4]^{2-}$	150	91.0	120

Analyte	Groundwater MS Amount (mg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	15	98.0	111
$[Cu(CN)_3]^{2-}$	0.5	90.4	127
$[Ag(CN)_2]^-$	75	98.7	114
$[Au(CN)_2]^-$	25	94.7	116
$[Co(CN)_6]^{3-}$	75	95.5	108
$[Ni(CN)_4]^{2-}$	150	97.4	110

Analyte	Wastewater MS Amount (mg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	15	87.1	117
$[Cu(CN)_3]^{2-}$	0.5	43.0	112
$[Ag(CN)_2]^-$	75	28.4	145
$[Au(CN)_2]^-$	25	69.4	120
$[Co(CN)_6]^{3-}$	75	93.3	109
$[Ni(CN)_4]^{2-}$	150	92.5	112

Analyte	Drinking Water MS Amount (mg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	15	101	109
$[Cu(CN)_3]^{2-}$	0.5	70.2	156
$[Ag(CN)_2]^-$	75	101	113
$[Au(CN)_2]^-$	25	97.8	112
$[Co(CN)_6]^{3-}$	75	97.8	109
$[Ni(CN)_4]^{2-}$	150	95.1	114

Analyte	Surface Water MS Amount (mg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	15	98.1	111
$[Cu(CN)_3]^{2-}$	0.5	76.4	151
$[Ag(CN)_2]^-$	75	97.9	114
$[Au(CN)_2]^-$	25	98.2	112
$[Co(CN)_6]^{3-}$	75	97.3	110
$[Ni(CN)_4]^{2-}$	150	97.9	110

Analyte	Reagent Water MS Amount (µg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	10	80.7	115
$[Cu(CN)_3]^{2-}$	4	80.7	127
$[Ag(CN)_2]^-$	100	44.6	137
$[Au(CN)_2]^-$	75	89.3	115
$[Co(CN)_6]^{3-}$	100	80.5	113
$[Ni(CN)_4]^{2-}$	75	83.2	115

TABLE 15 Determination of Precision and Bias
Analyte: $[Au(CN)_2]^-$

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (µg/L)	S_t (µg/L)	Bias
Reagent Water	15	16.47	6			1.14	9.8%
	18	18.46	6	6	0.98	1.37	2.5%
	57	58.49	6			3.91	2.6%
	60	64.07	6	6	3.00	4.11	6.8%
	85	87.04	5			0.63	2.4%
	90	90.10	6	5	1.58	4.81	0.1%
Wastewater	15	10.34	5			5.99	-31.1%
	18	13.93	4	4	0.49	1.70	-22.6%
	57	40.21	6			11.73	-29.5%
	60	42.68	6	6	2.47	13.85	-28.9%
	85	51.19	6			25.98	-39.8%
	90	65.53	6	6	17.77	18.15	-27.2%
Surface Water	15	14.98	5			1.98	-0.1%
	18	16.89	6	5	0.33	3.76	-6.2%
	57	53.40	6			8.77	-6.3%
	60	56.36	6	6	1.75	6.82	-6.1%
	85	81.97	6			6.37	-3.6%
	90	85.28	6	6	1.48	7.19	-5.2%
Groundwater 1	15	12.50	5			2.66	-16.7%
	18	16.50	5	4	0.73	2.14	-8.4%
	57	54.91	6			9.15	-3.7%
	60	52.23	6	6	10.67	10.82	-12.9%
	85	77.67	6			9.69	-8.6%
	90	82.92	6	6	9.17	10.47	-7.9%
Groundwater 2	15	14.25	6			1.49	-5.0%
	18	17.14	5	5	0.77	2.28	-4.8%
	57	53.66	6			5.58	-5.9%
	60	56.16	6	6	4.12	6.63	-6.4%
	85	82.05	6			4.72	-3.5%
	90	84.58	6	6	2.75	8.31	-6.0%
Drinking Water	15	16.56	6			1.10	10.4%
	18	17.96	7	6	1.06	2.40	-0.2%
	57	60.59	7			3.52	6.3%
	60	63.34	6	6	2.41	4.69	5.6%
	85	90.63	7			6.09	6.6%
	90	97.06	7	7	4.06	10.24	7.8%

Analyte	Wastewater MS Amount (µg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	10	66.4	115
$[Cu(CN)_3]^{2-}$	4	D	606
$[Ag(CN)_2]^-$	100	14.6	41.5
$[Au(CN)_2]^-$	75	19.6	117
$[Co(CN)_6]^{3-}$	100	81.7	106
$[Ni(CN)_4]^{2-}$	75	D	87.5

Analyte	Surface Water MS Amount (µg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	10	70.4	129
$[Cu(CN)_3]^{2-}$	4	D	341
$[Ag(CN)_2]^-$	100	16.8	81.1
$[Au(CN)_2]^-$	75	67.7	122
$[Co(CN)_6]^{3-}$	100	77.8	117
$[Ni(CN)_4]^{2-}$	75	31.8	157

Analyte	Groundwater MS Amount (µg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	10	81.6	124
$[Cu(CN)_3]^{2-}$	4	D	85.8
$[Ag(CN)_2]^-$	100	39.8	74.7
$[Au(CN)_2]^-$	75	70.7	119
$[Co(CN)_6]^{3-}$	100	87.2	111
$[Ni(CN)_4]^{2-}$	75	25.4	128

Analyte	Drinking Water MS Amount (µg/L)	Lower Recovery Limit (%)	Higher Recovery Limit (%)
$[Fe(CN)_6]^{4-}$	10	77.3	133
$[Cu(CN)_3]^{2-}$	4	D	599
$[Ag(CN)_2]^-$	100	49.7	115
$[Au(CN)_2]^-$	75	78.8	135
$[Co(CN)_6]^{3-}$	100	81.9	124
$[Ni(CN)_4]^{2-}$	75	19.6	179

16.8 One Matrix Duplicate (MD) should be analyzed with each sample laboratory-defined batch to test method precision. If non-detects are suspected in all samples to be analyzed, a Matrix Spike Duplicate (MSD) should be analyzed instead. The MD or MSD should be prepared in accordance with the guidelines outlined in Guides D5810 and D3856. The precision of the duplicate analysis should be compared, according to Practice D5847, to the nearest tabulated S_o value established from the interlaboratory precision and bias study data for each analyte.

16.9 In order to verify the quantitative values produced by the test method, an Independent Reference Material (IRM) submitted to the laboratory as a regular sample (if practical),

TABLE 16 Determination of Precision and Bias
Analyte: $[Co(CN)_6]^{3-}$

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (µg/L)	S_t (µg/L)	Bias
Reagent Water	12	12.46	7			0.88	3.9%
	14	14.05	7	7	0.45	1.44	0.3%
	95	90.48	7			7.06	-4.8%
	105	102.92	7	7	3.74	3.47	-2.0%
	180	173.95	7			12.40	-3.4%
	190	182.39	7	7	9.87	7.99	-4.0%
Wastewater	12	13.25	6			2.13	10.4%
	14	13.78	6	6	1.11	0.90	-1.6%
	95	89.54	6			4.70	-5.7%
	105	98.80	6	6	1.70	4.51	-5.9%
	180	167.62	5			7.24	-6.9%
	190	177.51	5	5	1.52	6.21	-6.6%
Surface Water	12	13.32	6			1.88	11.0%
	14	14.89	6	6	0.22	1.99	6.4%
	95	91.26	6			6.85	-3.9%
	105	103.22	6	6	4.89	6.92	-1.7%
	180	175.62	6			9.72	-2.4%
	190	182.01	6	6	3.45	12.34	-4.2%
Groundwater 1	12	14.20	6			3.41	18.4%
	14	15.83	6	6	0.87	4.19	13.1%
	95	94.05	6			5.69	-1.0%
	105	101.59	6	6	1.59	4.39	-3.2%
	180	174.12	6			9.83	-3.3%
	190	183.08	6	6	4.02	8.31	-3.6%
Groundwater 2	12	12.96	6			1.49	8.0%
	14	14.67	5	5	0.34	1.61	4.8%
	95	93.61	6			5.42	-1.5%
	105	104.31	6	6	1.81	3.30	-0.7%
	180	176.25	6			7.52	-2.1%
	190	189.16	6	6	2.70	4.52	-0.4%
Drinking Water	12	13.94	6			0.89	16.2%
	14	16.56	6	6	1.75	2.01	18.3%
	95	101.14	6			5.52	6.5%
	105	108.09	6	6	7.05	9.53	2.9%
	180	184.22	6			7.19	2.3%
	190	199.59	6	6	10.05	15.60	5.0%

should be analyzed once per quarter. The concentration of the IRM should be within the scope of the method as defined in Section 1. The values obtained must fall within the limits specified by the outside source.

16.10 The laboratory may perform additional quality control as desired or required for regulatory reporting. In addition, it is recommended that a laboratory determine the method detection limits, as discussed in 15.7, before using this test method.

17. Keywords

17.1 anion exchange chromatography; cobalt cyanide; copper cyanide; cyanide; drinking water; ferricyanide; ferrocyanide; free cyanide; gold cyanide; groundwater; iron cyanide; metal cyanide complexes; nickel cyanide; silver cyanide; surface water; total cyanide; wastewater

TABLE 17 Determination of Precision and Bias
Analyte: $[Ni(CN)_4]^{2-}$

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Reatined Samples	Number of Retained Youden Pairs	S_o (µg/L)	S_t (µg/L)	Bias
Reagent Water	55	53.52	5			1.21	-2.7%
	60	59.31	6	5	2.53	3.98	-1.1%
	75	73.54	6			5.56	-2.0%
	80	78.47	5	5	3.25	1.32	-1.9%
	90	90.75	6			5.79	0.8%
	95	95.72	6	6	5.50	6.86	0.8%
Wastewater	55	7.47	4			4.83	-86.4%
	60	4.72	4	4	3.55	3.89	-92.1%
	75	4.89	4			3.93	-93.5%
	80	19.97	3	2	2.50	32.47	-75.0%
	90	9.35	5			5.02	-89.6%
	95	21.92	5	4	1.12	30.18	-76.9%
Surface Water	55	56.46	6			17.64	2.7%
	60	62.15	6	6	1.88	19.00	3.6%
	75	65.09	6			10.44	-13.2%
	80	73.60	6	6	4.51	14.30	-8.0%
	90	85.58	6			14.75	-4.9%
	95	85.48	6	6	2.95	14.66	-10.0%
Groundwater 1	55	54.42	6			14.83	-1.1%
	60	56.62	6	6	6.21	15.31	-5.6%
	75	70.70	6			6.09	-5.7%
	80	70.60	5	5	5.29	2.08	-11.7%
	90	82.83	6			1.65	-8.0%
	95	81.62	6	6	8.19	11.66	-14.1%
Groundwater 2	55	43.32	6			9.97	-21.2%
	60	39.20	6	6	15.25	19.34	-34.7%
	75	55.89	6			8.81	-25.5%
	80	59.92	6	6	2.93	6.57	-25.1%
	90	71.95	6			10.24	-20.1%
	95	79.89	6	6	9.42	12.41	-15.9%
Drinking Water	55	49.92	6			24.47	-9.2%
	60	51.46	6	6	5.47	19.92	-14.2%
	75	69.24	6			14.94	-7.7%
	80	86.01	6	6	20.87	22.98	7.5%
	90	87.65	6			14.89	-2.6%
	95	87.19	6	6	6.87	21.07	-8.2%

TABLE 18 Summary of Precision and Bias Results for Reagent Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	1 to 18.5	0.2 to 1.7	21 to 90
Mean Recovery (mg/L)	1.0458 x + 0.0458 R^2 = 1.000	1.1306 x + -0.0102 R^2 = 0.998	1.0212 x + 2.2470 R^2 = 0.999
S_o (mg/L)	0.0123 x + 0.0149 R^2 = 1.000	0.0154 x + 0.0106 R^2 = 0.777	0.0131 x + 0.1147 R^2 = 0.743
S_t (mg/L)	0.0233 x + 0.00181 R^2 = 0.734	0.0819 x + 0.00014 R^2 = 0.844	0.00784 x + 1.10187 R^2 = 0.596
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	10 to 42	15 to 90	20 to 185
Mean Recovery (mg/L)	1.0159 x + 0.8670 R^2 = 0.999	1.0052 x + 0.8476 R^2 = 1.000	1.0480 x + 1.3162 R^2 = 1.000
S_o (mg/L)	-0.0040 x + 0.8385 R^2 = 0.013	0.0064 x + 0.0486 R^2 = 0.831	0.0118 x + -0.0211 R^2 = 0.891
S_t (mg/L)	0.0083 x + 0.67105 R^2 = 0.038	0.0105 x + 0.0513 R^2 = 0.479	0.0520 x + -0.9076 R^2 = 0.893

TABLE 19 Summary of Precision and Bias Results for Wastewater

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	1 to 18.5	0.2 to 1.7	21 to 90
Mean Recovery (mg/L)	1.0236 x + -0.0251 R^2 = 1.000	1.0513 x + -0.1375 R^2 = 0.999	0.8839 x + -1.4349 R^2 = 0.999
S_o (mg/L)	0.0201 x + 0.0160 R^2 = 0.960	0.0189 x + 0.0192 R^2 = 0.233	0.0079 x + 1.0890 R^2 = 0.316
S_t (mg/L)	0.0516 x + -0.0341 R^2 = 0.842	0.0520 x + 0.0375 R^2 = 0.924	0.2436 x + -1.2722 R^2 = 0.987
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	10 to 42	15 to 90	20 to 185
Mean Recovery (mg/L)	0.9524 x + -0.998 R^2 = 0.998	1.0010 x + 0.7879 R^2 = 1.000	1.0111 x + 1.6112 R^2 = 1.000
S_o (mg/L)	0.0412 x + -0.1301 R^2 = 0.988	0.0090 x + 0.1348 R^2 = 0.906	0.0120 x + 0.1431 R^2 = 0.995
S_t (mg/L)	0.0697 x + 0.4544 R^2 = 0.840	0.0237 x + 0.1591 R^2 = 0.951	0.0266 x + 0.7711 R^2 = 0.931

TABLE 20 Summary of Precision and Bias Results for Surface Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	1 to 18.5	0.2 to 1.7	21 to 90
Mean Recovery (mg/L)	1.0416 x + 0.0503 R^2 = 1.000	1.1223 x + 0.0080 R^2 = 1.000	1.0292 x + 2.1505 R^2 = 1.000
S_o (mg/L)	0.0114 x + -0.0082 R^2 = 0.875	0.0114 x + 0.0110 R^2 = 1.000	0.0165 x + -0.2253 R^2 = 0.867
S_t (mg/L)	0.0209 x + -0.0071 R^2 = 0.867	0.0377 x + 0.0410 R^2 = 0.567	0.0124 x + 0.9970 R^2 = 0.923
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	10 to 42	15 to 90	20 to 185
Mean Recovery (mg/L)	1.0488 x + 0.0439 R^2 = 1.000	1.0216 x + 1.0756 R^2 = 1.000	1.0297 x + 1.7513 R^2 = 1.000
S_o (mg/L)	0.0073 x + 0.1883 R^2 = 0.892	0.0067 x + 0.1042 R^2 = 0.875	0.0135 x + -0.0429 R^2 = 0.875
S_t (mg/L)	0.00314 x + 0.49168 R^2 = 0.122	0.01686 x + 0.2572 R^2 = 0.949	0.01316 x + 1.05352 R^2 = 0.958

TABLE 21 Summary of Precision and Bias Results for Groundwater

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	1 to 18.5	0.2 to 1.7	21 to 90
Mean Recovery (mg/L)	1.0425 x + 0.0295 R^2 = 1.000	1.0683 x + 0.0098 R^2 = 0.999	1.0320 x + 2.5531 R^2 = 1.000
S_o (mg/L)	0.0028 x + 0.0268 R^2 = 0.741	0.0013 x + 0.0148 R^2 = 0.029	-0.0055 x + 0.8887 R^2 = 0.691
S_t (mg/L)	0.0213 x + -0.0087 R^2 = 0.897	0.0727 x + -0.0089 R^2 = 0.916	0.0212 x + 0.2705 R^2 = 0.912
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	10 to 42	15 to 90	20 to 185
Mean Recovery (mg/L)	1.0536 x + -0.0588 R^2 = 0.999	1.0082 x + 0.8412 R^2 = 1.000	1.0276 x + 1.5710 R^2 = 1.000
S_o (mg/L)	-0.0026 x + 0.8705 R^2 = 0.005	0.0003 x + 0.2054 R^2 = 0.045	0.0072 x + 0.1865 R^2 = 0.965
S_t (mg/L)	0.0054 x + 0.72436 R^2 = 0.058	0.02034 R^2 = 0.984	0.0124 x + 1.2933 R^2 = 0.536

TABLE 22 Summary of Precision and Bias Results for Drinking Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	1 to 18.5	0.2 to 1.7	21 to 90
Mean Recovery (mg/L)	1.0454 x + 0.0464 R^2 = 1.000	1.0922 x + 0.0194 R^2 = 0.997	1.0317 x + 2.7372 R^2 = 1.000
S_o (mg/L)	0.0064 x + -0.0013 R^2 = 0.840	0.0440 x + -0.0010 R^2 = 0.588	0.0071 x + 0.1664 R^2 = 0.903
S_t (mg/L)	0.0126 x + -5E-06 R^2 = 0.828	0.0709 x + 0.03138 R^2 = 0.561	0.00543 x + 1.03253 R^2 = 0.247
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	8	8	8
Range Tested (mg/L)	10 to 42	15 to 90	20 to 185
Mean Recovery (mg/L)	1.0687 x + -0.4620 R^2 = 1.000	1.0195 x + 1.0479 R^2 = 1.000	1.0380 x + 1.0668 R^2 = 1.000
S_o (mg/L)	0.0139 x + -0.0014 R^2 = 0.995	0.0041 x + 0.1582 R^2 = 0.970	0.0052 x + 0.2631 R^2 = 1.000
S_t (mg/L)	0.0065 x + 0.43067 R^2 = 0.273	0.0171 x + 0.0498 R^2 = 0.980	0.0279 x + 0.3159 R^2 = 0.873

TABLE 23 Summary of Precision and Bias Results for Reagent Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	1.6 to 18	1.1 to 4.6	20 to 115
Mean Recovery (µg/L)	0.9650 x + 0.1173 R^2 = 1.000	0.9996 x + 0.1649 R^2 = 0.948	0.8025 x + 10.7361 R^2 = 0.991
S_o (µg/L)	0.0603 x + -0.1209 R^2 = 0.923	-0.0507 x + 0.4579 R^2 = 0.572	0.0112 x + 3.2189 R^2 = 0.041
S_t (µg/L)	0.0593 x + -0.0125 R^2 = 0.810	-0.0315 x + 0.4425 R^2 = 0.114	0.09382 x + 6.93996 R^2 = 0.771
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	15 to 90	12 to 190	55 to 95
Mean Recovery (µg/L)	1.0040 x + 1.3890 R^2 = 0.998	0.9591 x + 0.7728 R^2 = 1.000	1.0480 x + -4.2542 R^2 = 0.998
S_o (µg/L)	0.0109 x + 1.2440 R^2 = 0.143	0.0534 x + -0.8113 R^2 = 0.964	0.0824 x + -2.6915 R^2 = 0.868
S_t (µg/L)	0.0260 x + 1.25604 R^2 = 0.211	0.0510 x + 0.4739 R^2 = 0.786	0.0992 x + -3.4024 R^2 = 0.436

TABLE 24 Summary of Precision and Bias Results for Waste Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	1.6 to 18	1.1 to 4.6	20 to 115
Mean Recovery (µg/L)	0.8529 x + 0.5211 R^2 = 0.995	0.1154 x + 6.1770 R^2 = 0.080	0.2478 x + 3.3144 R^2 = 0.952
S_o (µg/L)	0.0424 x + 0.2292 R^2 = 0.477	0.1606 x + 0.3958 R^2 = 0.475	0.1024 x + -2.0944 R^2 = 0.944
S_t (µg/L)	0.0304 x + 0.5290 R^2 = 0.202	0.0908 x + 5.2697 R^2 = 0.046	0.0994 x + 1.68935 R^2 = 0.964
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	15 to 90	12 to 190	55 to 95
Mean Recovery (µg/L)	0.6605 x + 1.5383 R^2 = 0.971	0.9248 x + 1.5559 R^2 = 1.000	0.3160 x + -12.5750 R^2 = 0.436
S_o (µg/L)	0.2276 x + -5.8384 R^2 = 0.758	0.0024 x + 1.1957 R^2 = 0.486	-0.0685 x + 7.7591 R^2 = 0.974
S_t (µg/L)	0.2480 x + -0.5306 R^2 = 0.841	0.0299 x + 1.3073 R^2 = 0.926	0.4875 x + -23.5829 R^2 = 0.312

TABLE 25 Summary of Precision and Bias Results for Surface Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	1.6 to 18	1.1 to 4.6	20 to 115
Mean Recovery (µg/L)	0.9990 x + -0.0255 R^2 = 1.000	0.0199 x + 3.5305 R^2 = 0.000	0.4991 x + -0.9956 R^2 = 0.991
S_o (µg/L)	0.0580 x + -0.0724 R^2 = 0.927	-0.1803 x + 0.9226 R^2 = 0.640	0.0742 x + -0.0357 R^2 = 0.967
S_t (µg/L)	0.1138 x + -0.1583 R^2 = 0.787	-0.3100 x + 4.46201 R^2 = 0.042	0.11994 x + 4.8480 R^2 = 0.779
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	15 to 90	12 to 190	55 to 95
Mean Recovery (µg/L)	0.9506 x + -0.0131 R^2 = 0.999	0.9575 x + 1.6106 R^2 = 1.000	0.7420 x + 15.1253 R^2 = 0.929
S_o (µg/L)	0.0172 x + 0.2276 R^2 = 0.674	0.0188 x + 0.9175 R^2 = 0.477	0.0361 x + 0.2845 R^2 = 0.231
S_t (µg/L)	0.0596 x + 2.5866 R^2 = 0.589	0.05319 x + 1.3329 R^2 = 0.971	-0.1002 x + 22.7332 R^2 = 0.289

TABLE 26 Summary of Precision and Bias Results for Groundwater 1

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	1.6 to 18	1.1 to 4.6	20 to 115
Mean Recovery (µg/L)	0.6938 x + 0.5245 R^2 = 0.980	0.7616 x + 1.1879 R^2 = 0.624	0.3448 x + 5.7096 R^2 = 0.967
S_o (µg/L)	0.0560 x + 0.5511 R^2 = 0.999	1.3677 x + -1.9072 R^2 = 0.968	0.0447 x + 2.0706 R^2 = 0.427
S_t (µg/L)	0.2010 x + 0.0903 R^2 = 0.820	1.2226 x + 0.1926 R^2 = 0.406	0.1154 x + 8.3646 R^2 = 0.863
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	15 to 90	12 to 190	55 to 95
Mean Recovery (µg/L)	0.9260 x + -0.7065 R^2 = 0.996	0.9506 x + 2.7159 R^2 = 1.000	0.7419 x + 13.2070 R^2 = 0.971
S_o (µg/L)	0.1249 x + -0.1386 R^2 = 0.711	0.0178 x + 0.3292 R^2 = 0.898	0.0511 x + 2.5642 R^2 = 0.367
S_t (µg/L)	0.11356 x + 1.33808 R^2 = 0.831	0.03004 x + 2.9853 R^2 = 0.819	-0.2368 x + 26.5614 R^2 = 0.374

TABLE 27 Summary of Precision and Bias Results for Groundwater 2

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	1.6 to 18	1.1 to 4.6	20 to 115
Mean Recovery (µg/L)	0.9853 x + 0.4390 R^2 = 0.999	0.1485 x + 0.5920 R^2 = 0.881	0.5685 x + 0.4173 R^2 = 0.998
S_o (µg/L)	0.0372 x + 0.1183 R^2 = 0.701	-0.0050 x + 0.1971 R^2 = 0.009	0.0056 x + 1.1127 R^2 = 0.709
S_t (µg/L)	0.0221 x + 0.4826 R^2 = 0.093	0.0294 x + 0.7139 R^2 = 0.100	0.0756 x + 1.4936 R^2 = 0.935
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	15 to 90	12 to 190	55 to 95
Mean Recovery (µg/L)	0.9499 x + -0.1456 R^2 = 0.999	0.9826 x + 0.8911 R^2 = 1.000	0.9682 x + -15.0569 R^2 = 0.953
S_o (µg/L)	0.0309 x + 0.8153 R^2 = 0.439	0.0135 x + 0.2281 R^2 = 0.986	-0.1909 x + 24.1589 R^2 = 0.296
S_t (µg/L)	0.0698 x + 1.05409 R^2 = 0.742	0.02504 x + 1.4881 R^2 = 0.686	-0.0875 x + 17.8577 R^2 = 0.100

TABLE 28 Summary of Precision and Bias Results for Drinking Water

	$[Fe(CN)_6]^{4-}$	$[Cu(CN)_2]^{2-}$	$[Ag(CN)_2]^{-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	1.6 to 18	1.1 to 4.6	20 to 115
Mean Recovery (µg/L)	0.9840 x + 0.6402 R^2 = 0.999	0.8883 x + 2.9357 R^2 = 0.468	0.7339 x + 5.6643 R^2 = 0.984
S_o (µg/L)	0.0483 x + 0.0618 R^2 = 0.988	0.3354 x + -0.1664 R^2 = 0.984	0.0016 x + 2.0857 R^2 = 0.002
S_t (µg/L)	0.0313 x + 0.58685 R^2 = 0.607	0.6045 x + 2.39411 R^2 = 0.141	0.11858 x + 1.10313 R^2 = 0.656
	$[Au(CN)_2]^{-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$
Number of Laboratories	7	7	7
Range Tested (µg/L)	15 to 90	12 to 190	55 to 95
Mean Recovery (µg/L)	1.0774 x + -0.6713 R^2 = 1.000	1.0273 x + 1.8728 R^2 = 0.999	1.0692 x + -9.1706 R^2 = 0.914
S_o (µg/L)	0.0410 x + 0.2124 R^2 = 0.976	0.0473 x + 1.4157 R^2 = 0.981	0.0794 x + 4.8512 R^2 = 0.027
S_t (µg/L)	0.0903 x + -0.219 R^2 = 0.799	0.0598 x + 0.8478 R^2 = 0.753	-0.1001 x + 27.3026 R^2 = 0.157

TABLE 29 Pooled MDL Values Obtained for This Test Method

Analyte	Injected Amount (mg/L)	Mean Value (mg/L)	Pooled MDL (mg/L)
$[Fe(CN)_6]^{4-}$	0.5	0.56	0.09
$[Cu(CN)_3]^{2-}$	0.1	0.10	0.09
$[Ag(CN)_2]^{-}$	5.0	5.53	0.77
$[Au(CN)_2]^{-}$	5.0	5.29	0.64
$[Co(CN)_6]^{3-}$	5.0	5.36	0.43
$[Ni(CN)_4]^{2-}$	5.0	5.38	0.83

TABLE 30 Pooled MDL Values Obtained for This Test Method Using On-Line Sample Preconcentration

Analyte	Injected Amount (µg/L)	Mean Value (µg/L)	Pooled MDL (µg/L)
$[Fe(CN)_6]^{4-}$	1.0	1.02	0.21
$[Cu(CN)_3]^{2-}$	0.8	0.31	4.56
$[Ag(CN)_2]^{-}$	15.0	4.15	8.66
$[Au(CN)_2]^{-}$	10.0	8.97	2.80
$[Co(CN)_6]^{3-}$	10.0	10.16	0.99
$[Ni(CN)_4]^{2-}$	50.0	37.95	7.33

APPENDIX

(Nonmandatory Information)

X1. NON-PRECONCENTRATION FOR ICP-MS ANALYSIS

TABLE X1.1 Selected Isotopes for Analyte Quantitation Using ICP-MS Detection

Element	Fe	Ni	Co	Cu	Ag	Au
Isotope	56	58	59	63	107	197

X1.1 Trace determination of metal cyanide complexes using anion exchange chromatography is possible without the need for sample preconcentration if an inductively coupled plasma mass spectrometer (ICP-MS) equipped with a dynamic reaction cell (DRC) is used for detection after chromatographic separation. The extreme sensitivity of this detector and its capability of removing possible interferences make it a practical detector for anion exchange chromatography analysis.

X1.2 Single laboratory validation testing was performed in order to compare results obtained using anion exchange chromatography-ICP-MS detection with those obtained from the round robin collaborative study based on on-line sample preconcentration and UV absorption detection. For anion exchange chromatography using ICP-MS detection, analyte separation was performed as described within this test method using a 0.1 mL injection volume. Analyte detection was accomplished using a DRC ICP-MS instrument.[8] The chromatography ICP-MS interface was achieved by connecting the outlet of the analytical column to the inlet of the ICP nebulizer using PEEK tubing. Parameters such as nebulizer gas flow and lens voltage were optimized daily using a solution that contained all analytes. Ammonia gas was successfully used in the DRC to eliminate the high background on some analytes such as Fe, Ni, etc. The DRC parameters were optimized for each specific element. For confirmation purposes, two isotopes were monitored for each element, with the exception of Au and Co, which are monoisotopic. Quantitation was achieved using the most abundant isotopes for each element. The selected isotopes are listed in Table X1.1. Data acquisition was achieved using the ICP-MS instrument software. For analyte quantitation, raw time versus intensity data for each species was processed using chromatography instrument software.[9]

X1.3 For the anion exchange chromatography-UV detection method with on-line sample preconcentration , data from 7 laboratories was used for the precision and bias analyses following Practice D2777 procedures, the results of which are outlined in Tables 12-17 and Tables 23-28 of the test method (Section 15). The single laboratory anion exchange chromatography-ICP-MS data was analyzed separately using the following procedure pre-approved by the ASTM Results Advisor:

Step 1: For each analyte and matrix, the average bias was calculated across the six concentration measurements (three Youden pairs) using the equation:

$$\text{AvgBias} = <\frac{C_M}{C_T}> - 1 \qquad \text{(X1.1)}$$

where:

$< >$ = indicates average,
C_M = measured concentration, and
C_T = "true" concentration.

Step 2: For each analyte and matrix, the StDev, the standard deviation of the quantity C_M/C_T, was then calculated.

Step 3: The AvgBias and StDev for the seven laboratories taking part in the round robin study were then pooled to create a range of bias and overall standard deviation values.

Step 4: The AvgBias was then compared to the range of bias values obtained from the pooled data set from the rest of the laboratories.

Step 5: The StDev was then compared to the range of the overall standard deviation (S_t) values obtained from the pooled data set.

NOTE X1.1—A comparison of the single laboratory values with the ranges obtained from the pooled data from the seven laboratories provides a qualitative indication of how the two methods compare vis-à-vis the methods' precision and bias.

Step 6: The individual MDL of the seven laboratories taking part in the round robin study were pooled and the pooled MDL was compared to the MDL values calculated from the single laboratory to evaluate whether the single laboratory's MDL values were less than or equal to the pooled values.

NOTE X1.2—Table X1.2 provides the comparison of the single laboratory precision (StDev) and bias data with the pooled precision (StDev) and bias from the seven laboratories participating in the ppb-level round robin study (Section 15). Table X1.3 provides the comparison of the single laboratory MDL data with the pooled MDL from the ppb-level round robin study (Section 15).

X1.4 Based on the comparison between the single laboratory results and the results from the ppb level round robin study, no significant differences were observed between the two detection techniques used for quantifying the six metal cyanide complexes in the various water matrices tested.

[8] Perkin Elmer 6100 DRCPlus ICP-MS.
[9] Perkin Elmer Turbochrom Software.

TABLE X1.2 Comparison of Single Laboratory Anion Exchange Chromatography-ICP-MS Precision and Bias Data with Pooled Round Robin Anion Exchange Chromatography-UV Detection Precision and Bias Data

	$[Fe(CN)_6]^{4-}$		$[Cu(CN)_3]^{2-}$		$[Ag(CN)_2]^-$		$[Au(CN)_2]^-$		$[Co(CN)_6]^{3-}$		$[Ni(CN)_4]^{2-}$	
	min	max	min	max	min	max	min	max	min	max	min	max
						Reagent Water						
7-Labs Avg Bias Range	-6.2%	33.7%	-62.8%	41.5%	-33.3%	33.1%	-7.5%	8.7%	-9.5%	3.8%	-8.5%	5.1%
7-Labs Avg StDev Range	2.0%	18.0%	10.4%	57.9%	3.9%	37.8%	3.6%	8.5%	0.7%	12.9%	1.9%	8.9%
Single-Lab Avg Bias	-2.3%		118.2%		-49.2%		0.1%		-10.1%		-2.2%	
Single-Lab StDev	4.2%		108.0%		11.9%		7.3%		1.3%		1.7%	
Is Single-Lab Avg Bias Within Range?	yes		no		no		yes		no		yes	
Is Single-Lab StDev < Max?	yes		no		yes		yes		yes		yes	
						Wastewater						
7-Labs Avg Bias Range	-23.1%	34.4%	-34.4%	1006.5%	-89.5%	-43.7%	-69.7%	30.5%	-25.1%	9.0%	-100.0%	-13.6%
7-Labs Avg StDev Range	9.5%	52.5%	33.8%	645.3%	3.3%	79.4%	5.3%	77.2%	2.7%	55.5%	0.0%	76.6%
Single-Lab Avg Bias	5.5%		167.9%		-82.9%		9.1%		-8.4%		-84.5%	
Single-Lab StDev	13.3%		109.7%		15.6%		2.3%		1.3%		3.4%	
Is Single-Lab Avg Bias Within Range?	yes		yes		yes		yes		yes		yes	
Is Single-Lab StDev < Max?	yes		yes		yes		yes		yes		yes	
						Surface Water						
7-Labs Avg Bias Range	-6.3%	116.3%	-100.0%	1433.2%	-78.1%	-18.0%	-55.8%	4.5%	-10.6%	12.2%	-68.1%	28.8%
7-Labs Avg StDev Range	1.4%	124.5%	0.0%	433.1%	6.9%	25.5%	3.0%	35.9%	6.2%	14.2%	3.6%	21.4%
Single-Lab Avg Bias	4.2%		37.5%		-72.3%		-25.1%		-2.1%		-2.5%	
Single-Lab StDev	4.8%		170.7%		46.9%		8.3%		2.3%		9.1%	
Is Single-Lab Avg Bias Within Range?	yes		yes		yes		yes		yes		yes	
Is Single-Lab StDev < Max?	yes		yes		no		yes		yes		yes	
						Groundwater 1						
7-Labs Avg Bias Range	-52.7%	121.2%	-100.0%	811.7%	-89.4%	-11.5%	-16.0%	33.5%	-9.4%	18.0%	-21.8%	57.2%
7-Labs Avg StDev Range	3.4%	172.4%	0.0%	737.5%	5.0%	41.1%	2.3%	89.9%	2.2%	25.9%	5.3%	46.1%
Single-Lab Avg Bias	-8.8%		0.3%		-52.0%		-11.4%		-4.8%		24.7%	
Single-Lab StDev	9.2%		44.1%		31.5%		0.4%		1.9%		4.0%	
Is Single-Lab Avg Bias Within Range?	yes		yes		yes		yes		yes		yes	
Is Single-Lab StDev < Max?	yes		yes		yes		yes		yes		yes	
						Groundwater 2						
7-Labs Avg Bias Range	3.1%	56.1%	-100.0%	-6.1%	-78.7%	-19.0%	-42.1%	6.4%	-5.5%	7.9%	-34.8%	14.2%
7-Labs Avg StDev Range	8.6%	57.8%	0.0%	50.6%	1.7%	17.2%	2.5%	37.2%	3.5%	36.9%	6.6%	31.2%
Single-Lab Avg Bias	16.0%		-73.7%		-82.2%		-17.3%		-3.4%		-6.5%	
Single-Lab StDev	12.4%		25.5%		31.2%		7.2%		4.7%		2.1%	
Is Single-Lab Avg Bias Within Range?	yes		yes		no		yes		yes		yes	
Is Single-Lab StDev < Max?	yes		yes		no		yes		yes		yes	
						Drinking Water						
7-Labs Avg Bias Range	-96.9%	40.9%	-100.0%	562.9%	-87.8%	34.2%	-90.5%	7.7%	-88.8%	13.3%	-76.0%	25.3%
7-Labs Avg StDev Range	2.0%	51.9%	0.0%	528.6%	4.3%	34.5%	1.7%	39.6%	4.6%	17.1%	5.2%	50.1%
Single-Lab Avg Bias	5.0%		21.5%		-73.6%		-28.4%		-10.2%		0.9%	
Single-Lab StDev	2.7%		83.4%		10.6%		1.1%		1.8%		1.2%	
Is Single-Lab Avg Bias Within Range?	yes		yes		yes		yes		yes		yes	
Is Single-Lab StDev < Max?	yes		yes		yes		yes		yes		yes	

TABLE X1.3 Comparison of Single Laboratory Anion Exchange Chromatography-ICP-MS MDLs with Pooled Round Robin Anion Exchange Chromatography-UV Detection MDLs

	$[Fe(CN)_6]^{4-}$		$[Cu(CN)_3]^{2-}$		$[Ag(CN)_2]^-$		$[Au(CN)_2]^-$		$[Co(CN)_6]^{3-}$		$[Ni(CN)_4]^{2-}$	
	min	max	min	max	min	max	min	max	min	max	min	max
7-Labs MDL Range, µg/L	0.062	0.417	0.149	11.923	1.081	20.311	1.490	6.231	0.411	2.203	3.632	20.066
Single-Lab MDL, µg/L	0.193		6.271		2.805		0.698		0.402		2.194	
Is Single-Lab MDL < Max?	yes		yes		yes		yes		yes		yes	

REFERENCES

(1) Meeussen, J. C. L., Keizer, M. G., van Riemsdijk, W. H., and de Haan, F. A. M., "Dissolution Behavior of Iron Cyanide (Prussian Blue) in Contaminated Soils," *Environmental Science & Technology*, Vol 26, 1992, pp. 1832–1838.

(2) Meeussen, J. C. L., Keizer, W. H., and de Haan, F. A. M., "Chemical Stability and Decomposition Rate of Iron Cyanide Complexes in Soil Solutions," *Environmental Science & Technology*, Vol 26, 1992, pp. 511–516.

(3) Ghosh, R. S., Dzombak, D. A, and Luthy, R. G., "Equilibrium Precipitation and Dissolution of Iron Cyanide Solids in Water," *Environmental Engineering Science*, Vol 16, 1999, pp. 293–313.

(4) Dionex Corporation, "Determination of Metal Cyanides," Dionex Application Note No. 55, November, 1989.

(5) Wetzel, R. A., Anderson, C. L., Schleicher, H., and Crook, G. D., "Determination of Trace Level Ions by Ion Chromatography with Concentrator Columns," *Analytical Chemistry*., Vol 15, No. 9, 1979, pp. 1532–1535.

(6) Rader, W. S., Solujic, L., Milosavljevic, E. B., and Hendrix, J. L, "Sunlight-Induced Photochemistry of Aqueous Solutions of Hexacyanoferrate(II) and -(III) Ions," *Environmental Science & Technology*., Vol 27, 1993, pp. 1875–1879.

(7) Doudoroff, P., "Toxicity to Fish of Cyanides and Related Compounds: A Review," EPA Report No. 600/3-76-038, 1976.

(8) Moggi, L., Bolletta, F., Balzani, V., and Scandola, F., "Photochemistry of Co-ordination Compounds—XV," *Journal of Inorganic and Nuclear Chemistry*, Vol 28, 1966, pp. 2589–2597.

(9) Dionex Corporation, "Product Manual IonPac AG2 Guard Column IonPac AG3 Guard Column IonPac AG4 Guard Column IonPac AG5 Guard Column IonPac CG2 Guard Column IonPac AS2 Analytical Column IonPac AS3 Analytical Column IonPac AS4 Analytical Column IonPac AS5 Analytical Column IonPac CS2 Analytical Column," Document No. 032226, Revision 14, May 12, 2002.

(10) Dionex Corporation, "Installation and Troubleshooting Guide for the IonPac AG5 Guard Column IonPac AS11 Analytical Column," Document No. 034791, Revision 07, August 23, 2001.

(11) Dionex Corporation, "Product Manual IonPac ATC-3 2-mm Anion Trap Column IonPac ATC-3 4-mm Anion Trap Column IonPac ATC-HC Anion Trap Column," Document No. 032697, Revision 08, July 12, 2002.

(12) Dionex Corporation, "Installation Instructions and Troubleshooting Guide for the IonPac MFC-1 metal Free Trap Column," Document No. 034990, Revision 02, June 26, 1998.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D6994 – 10) that may impact the use of this standard. (Approved Oct. 1, 2010.)

(1) Added SI unit kPa to Section 7.

(2) Added filter information to Section 8.