



Designation: D6994 – 04

Standard Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection¹

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 12.1. 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 12.1. 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 *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

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits⁴

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 Good Laboratory Practices in Laboratories Engaged in Sampling and 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*—For a definition of terms used in this method, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *anion exchange chromatography*—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*—the liquid mobile phase used in anion exchange chromatography to transport the sample through the chromatography system.

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.

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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.

⁴ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

3.2.3 *analytical column*—the chromatography column that contains the stationary phase for separation by ion exchange. 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*—a short chromatography column that is placed before the analytical column to protect it from particulates and impurities that may cause fouling.

3.2.5 *anion trap column*—a high-capacity, low-pressure anion exchange column used to remove reagent impurities from the eluent stream. The anion trap column is placed between the eluent reservoir and the gradient pump.

3.2.6 *gradient elution*—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*—a liquid chromatography pump that is capable of performing gradient elutions.

3.2.8 *total cyanide*—the sum total of all of the inorganic chemical forms of cyanide. Total cyanide thus includes both free cyanide and anionic metal cyanide complexes.

3.2.9 *metal cyanide complex*—a negatively charged ionic complex consisting of one or more cyanide ions bound to a single transition metal cation. Also referred to as *metal-complexed cyanides*, these complexes have the general formula:



where:

M = transition metal cation,

b = number of cyanide groups, and

x = ionic charge of the transition metal complex.

3.2.9.1 *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.

3.2.9.2 *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*—the form of cyanide recognized as being bioavailable and toxic. 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 Methods

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 **12.1** 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 **12.1** 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).

NOTE 1—Caution: 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® 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 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 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 200 to 2000 psi.

7.1.5 *Chromatography Tubing*—The tubing must be pressure resistant (approximately 3000 psi) and made of a material that is compatible with the eluent solutions. Examples of suitable materials are 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 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

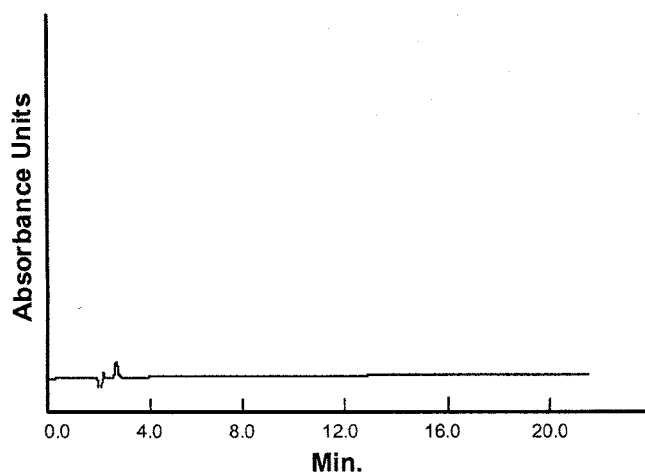


FIG. 1 Blank Chromatogram of Reagent Water

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 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 $\leq 100 \mu\text{g/L}$. 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 $[\text{Co}(\text{CN})_6]^{3-}$)—Dissolve exactly 1.5455 g of potassium cobalt cyanide, $\text{K}_3[\text{Co}(\text{CN})_6]$, 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 $[\text{Co}(\text{CN})_6]^{3-}$)—Dilute exactly 10 mL of $[\text{Co}(\text{CN})_6]^{3-}$ 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.

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 *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

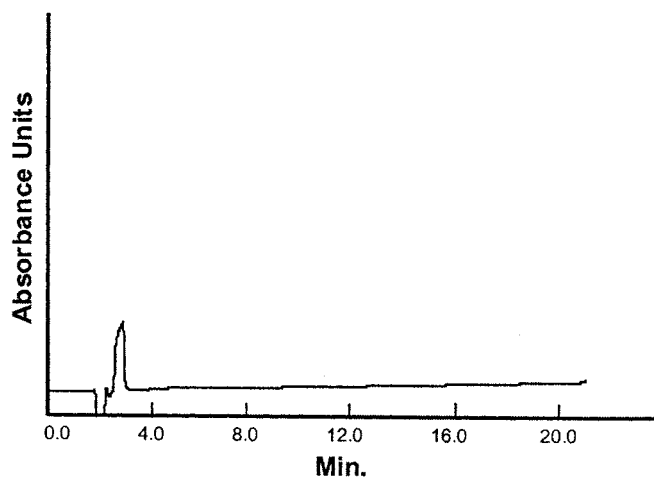


FIG. 2 Blank Chromatogram of Reagent Water Using On-line Sample Preconcentration

8.6 *Cobalt Cyanide II Solution, Standard* (1.00 mL = 10 μg $[\text{Co}(\text{CN})_6]^{3-}$)—Dilute exactly 10 mL of $[\text{Co}(\text{CN})_6]^{3-}$ 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.

8.7 *Cobalt Cyanide III Solution, Standard* (1.00 mL = 0.1 μg $[\text{Co}(\text{CN})_6]^{3-}$)—Dilute exactly 1 mL of $[\text{Co}(\text{CN})_6]^{3-}$ 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 $\text{Cu}[(\text{CN})_3]^{2-}$)—Combine exactly 0.6325 g of 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.

NOTE 2—**Warning:** NaCN is extremely toxic. Avoid inhalation and skin and eye contact (see 9.1.1).

NOTE 3—**Caution:** The copper cyanide will dissolve upon addition of sodium cyanide to form the cyanocuprate complex, $[\text{Cu}(\text{CN})_3]^{2-}$ that is the analyte of interest.

8.9 *Copper Cyanide I Solution, Standard* (1.00 mL = 100 μg $[\text{Cu}(\text{CN})_3]^{2-}$)—Dilute exactly 10 mL of $[\text{Cu}(\text{CN})_3]^{2-}$ 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 $[\text{Cu}(\text{CN})_3]^{2-}$)—Dilute exactly 10 mL of $[\text{Cu}(\text{CN})_3]^{2-}$ 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 $[\text{Cu}(\text{CN})_3]^{2-}$)—Dilute exactly 1 mL of $[\text{Cu}(\text{CN})_3]^{2-}$ 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 $\text{NaClO}_4 \cdot \text{H}_2\text{O}$)—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 $[\text{Au}(\text{CN})_2]^-$)—Dissolve exactly 1.1570 g of potassium gold cyanide, $\text{KAu}(\text{CN})_2$, 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 $[\text{Au}(\text{CN})_2]^-$)—Dilute exactly 10 mL of $[\text{Au}(\text{CN})_2]^-$ 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 $[\text{Au}(\text{CN})_2]^-$)—Dilute exactly 10 mL of $[\text{Au}(\text{CN})_2]^-$ 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 $[\text{Au}(\text{CN})_2]^-$)—Dilute exactly 1 mL of $[\text{Au}(\text{CN})_2]^-$ 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 $[\text{Fe}(\text{CN})_6]^{4-}$)—Dissolve exactly 1.9929 g of potassium ferrocyanide trihydrate, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, 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 $[\text{Fe}(\text{CN})_6]^{4-}$)—Dilute exactly 10 mL of $[\text{Fe}(\text{CN})_6]^{4-}$ 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 $[\text{Fe}(\text{CN})_6]^{4-}$)—Dilute exactly 10 mL of $[\text{Fe}(\text{CN})_6]^{4-}$ 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 $[\text{Fe}(\text{CN})_6]^{4-}$)—Dilute exactly 1 mL of $[\text{Fe}(\text{CN})_6]^{4-}$ 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 $[\text{Ni}(\text{CN})_4]^{2-}$)—Dissolve exactly $(1.4806 + 0.1107 \times n)$ g of potassium nickel cyanide mono- or polyhydrate, $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot n\text{H}_2\text{O}$ (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 $[\text{Ni}(\text{CN})_4]^{2-}$)—Dilute exactly 10 mL of $[\text{Ni}(\text{CN})_4]^{2-}$ 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 $[\text{Ni}(\text{CN})_4]^{2-}$)—Dilute exactly 10 mL of $[\text{Ni}(\text{CN})_4]^{2-}$ 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 $[\text{Ni}(\text{CN})_4]^{2-}$)—Dilute exactly 1 mL of $[\text{Ni}(\text{CN})_4]^{2-}$ 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 $[\text{Ag}(\text{CN})_2]^-$)—Dissolve exactly 1.2445 g of potassium silver cyanide, $\text{K}[\text{Ag}(\text{CN})_2]$, 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 $[\text{Ag}(\text{CN})_2]^-$)—Dilute exactly 10 mL of $[\text{Ag}(\text{CN})_2]^-$ 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 $[\text{Ag}(\text{CN})_2]^-$)—Dilute exactly 10 mL of $[\text{Ag}(\text{CN})_2]^-$ 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 $[\text{Ag}(\text{CN})_2]^-$)—Dilute exactly 1 mL of $[\text{Ag}(\text{CN})_2]^-$ 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 contamination.

NOTE 4—**Caution:** 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.

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 and Specification D1192, as applicable.

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

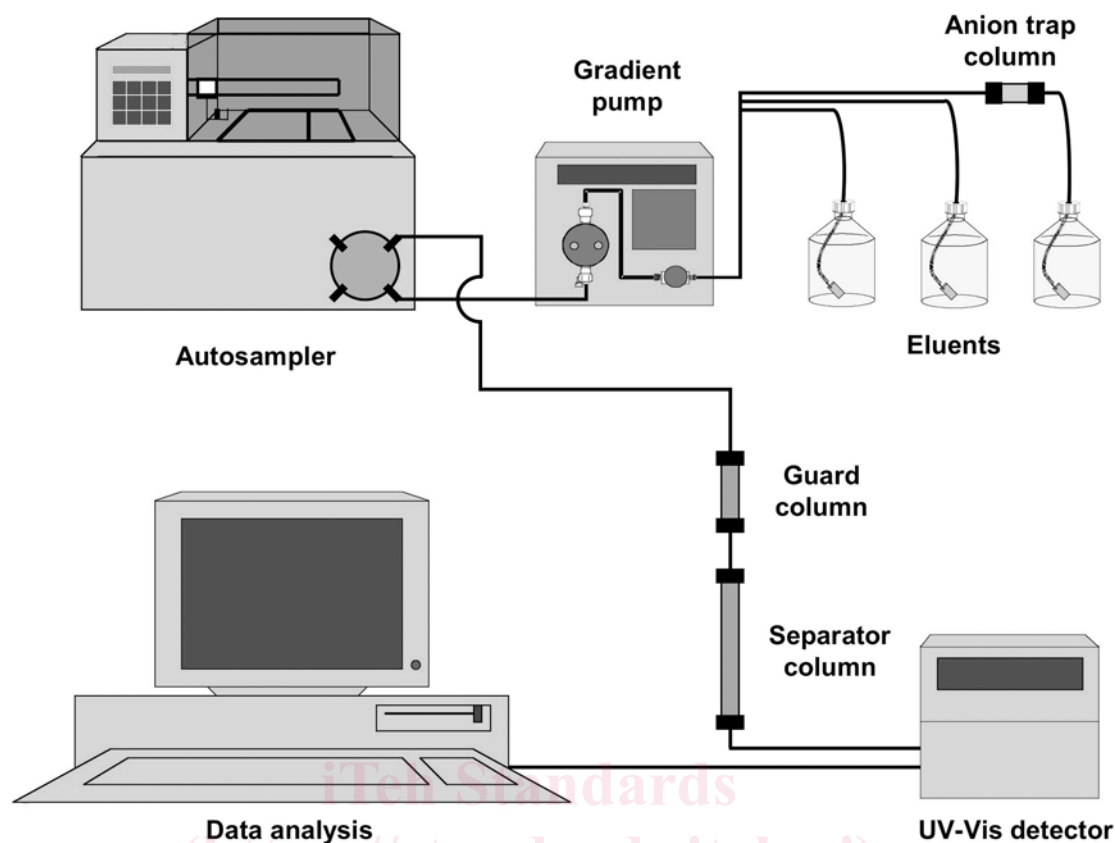


FIG. 3 Chromatograph Configuration for the Analysis of Metal Cyanides

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.

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.

NOTE 5—**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

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.

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.

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.

NOTE 6—Caution: 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.

NOTE 7—Caution: Eluent is pumped through the concentrator column by placing the injection valve in the “Inject” mode (see Fig. 5).

12. Calibration

NOTE 8—Caution: Since all iron cyanide complexes are detected as ferrocyanide ($[\text{Fe}(\text{CN})_6]^{4-}$), this form of iron cyanide is used in the preparation of the calibration standards.

12.1 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.

12.2 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.

NOTE 9—Caution: The calibration and subsequent analysis results for iron cyanide should be presented as either $[\text{Fe}(\text{CN})_6]^{x-}$ or $[\text{Fe}(\text{CN})_6]^{3-/4-}$ 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.

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

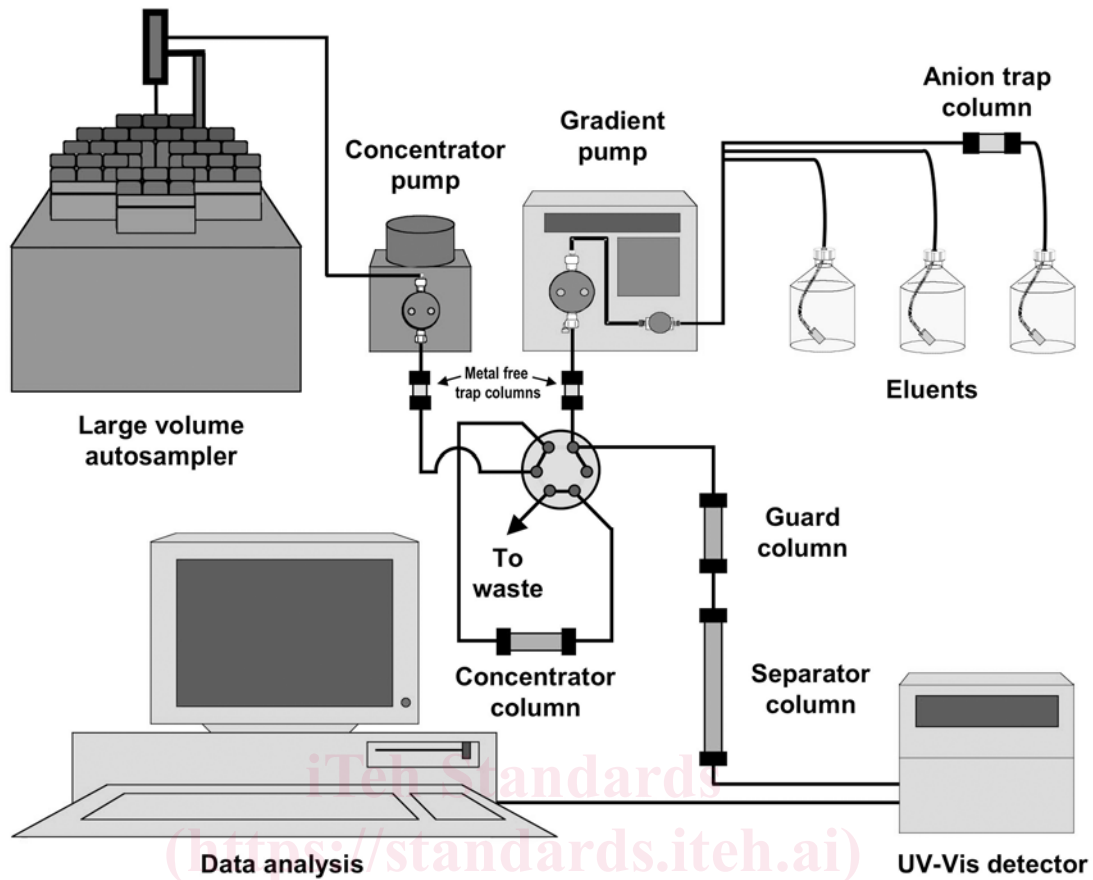


FIG. 4 Chromatograph Configuration for the Analysis of Metal Cyanides Using Sample Preconcentration

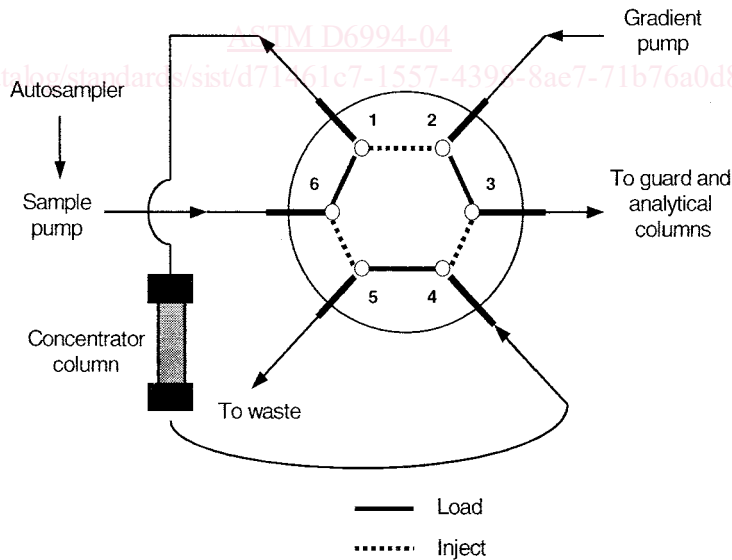


FIG. 5 Injection Valve Configuration for Sample Preconcentration

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

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

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.

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 12.2. Make the necessary adjustments to the final results based on any dilutions that were performed using the following calculation:

$$\frac{\mu\text{g or mg}}{\text{L}} [M(\text{CN})_b]^{x-} = \quad (2)$$

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

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:

$$\frac{\mu\text{g or mg}}{\text{L}} [M(\text{CN})_b]^{x-} \text{ as } \text{CN}^- = \quad (3)$$

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

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

15.1 The precision and bias data presented in this test method meets the requirements of Practice D2777. The full research report can be obtained from ASTM Headquarters.

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 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 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.