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METHOD 9015

METAL CYANIDE COMPLEXES IN WATERS AND WASTE EXTRACTS USING ANION EXCHANGE CHROMATOGRAPHY AND UV DETECTION

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of metal cyanide complexes in waters and extracts of solid wastes using anion exchange chromatography and UV detection (Refs. 1, 2). The following analytes have been determined by this method:

Analyte	Common Name
$[Ag(CN)_2]^-$	Dicyanoargentate(I)
$[Au(CN)_2]^-$	Dicyanoaurate(I)
$[Co(CN)_6]^{3-}$	Hexacyanocolbaltate(III)
$[Cu(CN)_3]^{2-}$	Tricyanocuprate(I)
$[Fe(CN)_6]^{3-}$	Hexacyanoferrate(III)[a]
$[Fe(CN)_6]^{4-}$	Hexacyanoferrate(II)[b]
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II)

[a]Also referred to as ferricyanide
[b]Also referred to as ferrocyanide

1.2 The use of alkaline sample preservation conditions for aqueous samples ensures that all metal cyanide species are solubilized and recovered in the analysis (Refs. 3-6).

1.3 Prior to the analysis of solid waste samples, the Method 9013 alkaline extraction procedure is necessary (Ref. 7). For the extract solutions to be analyzed by this method, the procedure in Sec. 11.2 needs to be performed after the Method 9013 extraction process.

1.4 This method may be applied to water and Method 9013 extract samples containing metal cyanide complexes with concentrations ranging from 0.2-200 mg/L (measured as $[M(CN)_b]^{x-}$, where M is the metal cation, b is the number of cyanide ions, and x is the overall

charge of the metal cyanide complex anion). This range will differ depending on the specific metal cyanide analyte, with some exhibiting greater or lesser detection sensitivity than others. Approximate calibration ranges are provided in Table 1. Concentrations greater than the specific analyte range may be determined after appropriate dilution.

1.5 Metal cyanide concentrations less than 0.2 mg/L may be determined through the use of on-line sample preconcentration coupled with anion exchange chromatography. Specific instructions for performing anion exchange chromatography analysis using sample preconcentration are given in Sec. 11.4. The concentration range for detection will vary depending on the specific metal cyanide analyte, with some exhibiting greater or lesser detection sensitivity than others. Approximate calibration ranges are provided in Table 2. The preconcentration method is not applicable for silver and copper cyanide complexes in matrices with total dissolved solids (TDS) greater than 1000 mg/L.

1.6 This test method is capable of resolving the metal cyanide complexes of iron, cobalt, silver, gold, copper, and nickel. The test method may also be applied to the determination of additional metal cyanide complexes, such as those of palladium and platinum. However, it is the responsibility of the user of this method to establish the validity of the test method for the determination of cyanide complexes of other metals.

1.7 This method cannot determine some weak metal cyanide complexes, such as zinc- and cadmium-cyanide complexes. These complexes elute very quickly and therefore cannot be differentiated from the solvent peak in the chromatogram.

1.8 This test method is not applicable for matrices with high ionic strength (conductivity greater than 70,000 μmhos/cm) or high TDS (greater than 30,000 mg/L).

1.9 The reactive cyanide content of a waste is not determined by this method and this method is not required by the RCRA regulations for the determination of the hazardous waste characteristic of reactivity. See 40 CFR 261.23 for information on the characteristic of reactivity.

1.10 This method is useful for the direct determination of metal cyanide complexes. The method is important from an environmental perspective in that it can differentiate between the cyanide species of limited toxicity and the highly toxic free cyanide (HCN and CN^-) that together make up total cyanide (Ref. 3). The toxicity of metal cyanide complexes is generally related to their ability to dissociate in the environment and release free cyanide (Ref. 8). Table 3 presents the log K stability constants for selected metal complex cyanides which may be used to provide an estimate of their relative environmental toxicity. Previous determinations of metal cyanide complexes have been made based on the assumption that the concentration is equivalent to the difference between total cyanide and free cyanide. This approach is subject to error because different methods used to determine free cyanide, such as the cyanides amenable to chlorination method (Ref. 9-11) or the weak-acid dissociable cyanide method (Refs. 10, 11) often provide widely varying results, thus impacting the metal cyanide complex concentration that is determined by difference. Direct analysis using anion exchange chromatography avoids these method biases and provides a more accurate and precise determination of metal cyanide complexes.

1.11 Prior to employing this method, analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and

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on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly required in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.12 This method is restricted to use by, or under supervision of, properly experienced and trained personnel knowledgeable of anion exchange chromatography and UV detection. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 For aqueous samples containing 0.2 - 200 mg/L metal cyanide complexes, dissolved metal cyanide complexes are separated and quantified using anion exchange chromatography coupled with UV detection. For solid waste samples, the alkaline extraction procedure described in Method 9013 is necessary prior to chromatographic analysis of the resulting extract. A sample volume is injected into the chromatograph and onto an anion exchange column where the metal cyanide analytes are separated from the sample matrix by temporary retention on the column. The metal cyanide complexes are eluted from the column by the eluent gradient and detected as signal peaks using UV absorbance at 215 nm. Their concentrations in the sample are determined by comparison of the analyte peak area with a standard calibration plot. The concentration range will differ depending on the specific metal cyanide complex, with some complexes exhibiting greater or lesser detection sensitivity than others based on their molar absorptivity. Under the alkaline conditions of the analysis, ferricyanide ($[Fe(CN)_6]^{3-}$) is reduced to ferrocyanide ($[Fe(CN)_6]^{4-}$) co-eluting as a single analyte peak, with any unreduced ferricyanide exhibited as tailing on the ferrocyanide peak.

2.2 For aqueous samples containing 0.5 - 200 µg/L metal cyanide complexes, dissolved metal cyanide complexes are determined using anion exchange chromatography coupled with on-line sample preconcentration (Ref. 12). For solid waste samples, the alkaline extraction procedure described in Method 9013 is necessary prior to chromatographic analysis of the resulting extract. A sample volume 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 onto an anion exchange column where the remainder of the analysis is completed as described in Sec. 2.1. The calibration range using sample preconcentration is nominally 0.5-200 µg/L metal cyanide complexes. This range will differ depending on the specific metal cyanide analyte, with some species exhibiting greater or lesser detection sensitivity than others based on their molar absorptivity.

2.3 Samples containing 200 µg/L - 0.5 mg/L metal cyanide complexes may either be analyzed using the preconcentration chromatography method after appropriate dilution or as described in Sec. 2.1, using a larger injection volume.

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3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. Although common anions will not interfere with the analysis, all materials that come into contact with samples must be demonstrated to be free from contaminants under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware.

4.2 Photodecomposition of some metal cyanide complexes such as those of iron can reduce their concentration (Refs. 13, 14). Collect samples so as to prevent exposure to light (see Sec. 8.1.). Store samples in amber, plastic/glass bottles before analysis and protect the samples from light whenever possible.

4.3 Carbonate is not a method interferent, but it 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. Take care to avoid carbonate contamination when preparing and using sodium hydroxide eluents.

CAUTION: Carbonate is formed in sodium hydroxide solutions by reaction with atmospheric carbon dioxide. Prepare all eluents using reagent water degassed with helium to prevent carbonate contamination as well as eluent outgassing during the analysis. Guidelines are provided in this test method for preparing low-carbonate sodium hydroxide eluent and reagent solutions.

4.4 Commercial grade sodium cyanide used in the preparation of Eluent 1 (Sec. 7.4) often contains complexed-metal cyanide impurities. These impurities can cause noisy, unstable baselines during the gradient elution profile. The installation of an anion trap column between Eluent 1 and the gradient pump removes the impurities from the eluent stream and results in improved chromatographic baselines. Guidelines for installing the anion trap column are provided in Sec. 11.6.

4.5 The Dionex IonPac® AG5, AG11, AS5, and AS11 chromatography columns referenced in this test method (Secs. 6.1.7, 6.1.8, and 6.2.4) 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 and of the column equilibration time. Sample preconcentration will enhance this effect. High purity reagent water free of organic contaminants should be used in the preparation of reagents.

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4.6 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 (Sec. 7.4) to form extraneous metal cyanide complexes. Metal-free trap columns should be installed to prevent positive interference by extraneous metal cyanide complexes when performing sample preconcentration (Sec. 6.2.5).

4.7 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.

4.8 Matrices with relatively high ionic strength (conductivity greater than 70,000 μmhos/cm) or total dissolved solids (TDS greater than 30,000 mg/L) will affect the performance of the analytical columns, resulting in poor separation and recovery of the metal cyanide complexes. Such samples, if encountered, cannot be analyzed by this method. However, this does not apply to most environmental samples, where the ionic strength and TDS are generally well below these levels.

4.9 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 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 (e.g., TDS greater than 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. Typically, only industrial process wastewaters have TDS levels exceeding 1000 mg/L. For such matrices, sample dilution using pH 12 reagent water (Sec. 7.8) can be used to lower the TDS level provided that the concentrations of the metal cyanide complexes of interest are not diluted below the lower limits of detection.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

WARNING: KCN and NaCN are highly toxic. Avoid skin and eye contact and inhalation.

5.2 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.

5.3 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. After analysis, collect the effluent and immediately adjust it to a pH of 12 or greater. Dispose of the effluent in an appropriate manner.

5.4 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Warnings are included for known extremely hazardous materials or procedures.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Anion exchange chromatography apparatus equipment

6.1.1 Pressurized eluent reservoir - Accessories must include a gas regulator capable of maintaining a 2-10 psi head pressure on the eluent solutions using helium gas.

6.1.2 Pressurizable eluent bottles - Bottles must be capable of withstanding an internal pressure of 7-10 psi. The bottles must be made of a chemically inert plastic such as polypropylene, suitable for use with sodium hydroxide-based eluents.

6.1.3 Tubing - To be used with the eluent reservoir and made of a material that is compatible with the eluent solutions.

6.1.4 Gradient pump - High performance liquid chromatography (HPLC) or ion chromatography (IC) pump capable of delivering a constant flow in the range of 1-5 mL/min at a pressure of 200-2000 psi.

6.1.5 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.

6.1.6 Anion trap column (ATC) - The ATC 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 x 24 mm) (Ref. 15) or equivalent. The column must be composed of a material appropriate for use with sodium hydroxide eluents.

6.1.7 Analytical column - Low-capacity anion exchange chromatography column. The selected column must provide for adequate selectivity of high valent metal cyanide complexes. Examples include the Dionex IonPac® AS5 (4-mm) (Ref. 16) and the Dionex IonPac® AS11 (4-mm or 2-mm) (Ref. 17) columns, or equivalent. These

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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 flow rate of a 4-mm column. Due to the decreased flow rate, the 2-mm column consumes only ¼ the eluent required by a 4-mm column.

6.1.8 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 must provide for adequate selectivity of highly valent metal cyanide species. Examples include the Dionex IonPac® AG5 (Ref. 16) and AG11 (Ref. 17) columns or equivalent.

6.1.9 Ultraviolet/Visible Spectroscopic (UV/Vis) detector - Liquid chromatography UV/Vis detector, capable of low wavelength detection at 215 nm.

6.1.10 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

6.2 On-line sample preconcentration accessories - Additional electrical contact closures are required for establishing automatic control of the preconcentration hardware accessories.

6.2.1 Injection valve - 2-way switching valve capable of injecting volumes ranging from 0.1 µL-1 mL.

6.2.2 Autosampler - Capable of handling 40-mL sample vials for use in performing sample preconcentration.

6.2.3 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.

6.2.4 Concentrator column - Low-capacity anion exchange chromatography concentrator column. The selected column must provide for adequate selectivity of highly valent transition metal cyanide species. Examples are the Dionex IonPac® AG5 (Ref. 16) and AG11 (Ref. 17) columns or equivalent.

6.2.5 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 Sec. 11.4.2.). An example is the Dionex IonPac® MFC-1 (Ref. 18) or equivalent. Refer to the manufacturer's instructions for column preparation and clean-up.

6.2.6 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 deliver a constant flow in the range of 1-5 mL/min at a pressure of 200 - 2000 psi.

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6.3 Amber reagent bottles - 100 mL and 1000 mL

6.4 Membrane syringe filters - 25 mm diameter, 0.2 - 0.45 mm pore size, having low background extractables, used to filter and remove sample particulates

6.5 Plastic syringes - 5 and 10 mL volumes

6.6 pH electrode, meter and calibration buffers or pH papers or test strips

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Whenever available, HPLC grade must be used in place of reagent grade. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers. Note, however, that sodium hydroxide solutions of relatively moderate strength (i.e., 4.1 g/L and greater), should be stored in HDPE plastic containers whenever possible.

7.2 Reagent water - ASTM Type I or deionized water, free of the analyte of interest. The reagent water should contain particles no larger than 0.20 µm. 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. Figures 1 and 2 provide examples of method blank chromatograms. All references to water in this method refer to reagent water as defined in Chapter One unless otherwise specified.

7.3 Degassed reagent water - Sparge reagent water with helium gas for approximately 20 min to remove dissolved gases such as carbon dioxide.

7.4 Eluent 1 (20 mM NaOH, 150 mM NaCN) - Place 1.6 g of sodium hydroxide solution (50% w/w) and 7.35 g of sodium cyanide into a 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 complex throughout the analysis.

WARNING: NaCN is extremely toxic. Avoid inhalation and skin and eye contact (See Sec. 5.0.).

7.5 Eluent 2 (20 mM NaOH, 300 mM $NaClO_4 \cdot H_2O$) - Place 1.6 g of sodium hydroxide solution (50% w/w) and 42.1 g of sodium perchlorate monohydrate into a 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.

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7.6 Eluent 3 (20 mM NaOH) - Place 1.6 g of sodium hydroxide solution (50% w/w) into a 1-L volumetric flask. Dilute to volume with degassed reagent water and mix thoroughly.

7.7 Sodium Hydroxide Solution I (50% w/w, 19.3 M) - 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 within the laboratory may result in carbonate contamination. This solution is used for the preparation of the eluents (Secs. 7.4 through 7.6) and Sodium Hydroxide Solution II (Sec. 7.8).

7.8 Sodium Hydroxide Solution II (10 mM, pH = 12) - Place 0.8 g of Sodium Hydroxide Solution I into a 1-L volumetric flask. Dilute to volume with degassed reagent water and mix thoroughly. Check to ensure that the pH is equal to 12 or greater using a pH paper/test strip or a calibrated pH electrode. Add additional Sodium Hydroxide Solution I, if needed, to bring the pH to 12.

NOTE: 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 or solid waste extracts. 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.

7.9 Method blank - Use Sodium Hydroxide Solution II (Sec. 7.8).

7.10 Cobalt Cyanide Stock Solution (1000 mg/L $[Co(CN)_6]^{3-}$) - Dissolve exactly 0.1182 g of potassium cobalt cyanide, $K_3[Co(CN)_6]$, with approximately 50 mL of Sodium Hydroxide Solution II in a 100-mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II and store at ≤6 ºC in an amber reagent bottle. The solution is relatively stable and may be stored for up to one month. Bring to room temperature prior to use.

7.11 Cobalt Cyanide Standard Solution I (100 mg/L $[Co(CN)_6]^{3-}$) - Dilute exactly 10 mL of $[Co(CN)_6]^{3-}$ Stock Solution (Sec. 7.10) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.12 Cobalt Cyanide Standard Solution II (10 mg/L $[Co(CN)_6]^{3-}$) - Dilute exactly 10 mL of $[Co(CN)_6]^{3-}$ Standard Solution I (Sec 7.11) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.13 Cobalt Cyanide Standard Solution III (100 µg/L $[Co(CN)_6]^{3-}$) - Dilute exactly 1 mL of $[Co(CN)_6]^{3-}$ Standard Solution II (Sec 7.12) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.14 Copper Cyanide Stock Solution (1000 mg/L $[Cu(CN)_3]^{2-}$) - Combine exactly 0.0632 g of copper cyanide, CuCN, with approximately 90 mL of Sodium Hydroxide Solution II in a 100-mL volumetric flask. Add exactly 0.0692 g of sodium cyanide, NaCN, and stir to dissolve both the copper cyanide and sodium cyanide. Dilute to volume with Sodium Hydroxide Solution II and store at ≤6 ºC in an amber reagent bottle. The solution may be stored for up to two weeks. Bring to room temperature prior to use.

NOTE: 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.

WARNING: NaCN is extremely toxic. Avoid inhalation and skin and eye contact (See Sec. 5.0.).

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7.15 Copper Cyanide Standard Solution I (100 mg/L $[Cu(CN)_3]^{2-}$) - Dilute exactly 10 mL of $[Cu(CN)_3]^{2-}$ Stock Solution (Sec. 7.14) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.16 Copper Cyanide Standard Solution II (10 mg/L $[Cu(CN)_3]^{2-}$) - Dilute exactly 10 mL of $[Cu(CN)_3]^{2-}$ Standard Solution I (Sec. 7.15) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.17 Copper Cyanide Standard Solution III (100 µg/L $[Cu(CN)_3]^{2-}$) - Dilute exactly 1 mL of $[Cu(CN)_3]^{2-}$ Standard Solution II (Sec. 7.16) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.18 Gold Cyanide Solution Stock Solution (1000 mg/L $[Au(CN)_2]^-$) - Dissolve exactly 0.1157 g of potassium gold cyanide, $K[Au(CN)_2]$, with approximately 50 mL of Sodium Hydroxide Solution II in a 100-mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II and store at ≤6 ºC in an amber reagent bottle. The solution is relatively stable and may be stored for up to one month. Bring to room temperature prior to use.

7.19 Gold Cyanide Standard Solution I (100 mg/L $[Au(CN)_2]^-$) - Dilute exactly 10 mL of $[Au(CN)_2]^-$ Stock Solution (Sec. 7.18) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.20 Gold Cyanide Standard Solution II (10 mg/L $[Au(CN)_2]^-$) - Dilute exactly 10 mL of $[Au(CN)_2]^-$ Standard Solution I (Sec. 7.19) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.21 Gold Cyanide Standard Solution III (100 µg/L $[Au(CN)_2]^-$) - Dilute exactly 1 mL of $[Au(CN)_2]^-$ Standard Solution II (Sec. 7.20) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.22 Iron Cyanide Solution Stock Solution (1000 mg/L $[Fe(CN)_6]^{4-}$) - Dissolve exactly 0.1993 g of potassium ferrocyanide trihydrate, $K_4[Fe(CN)_6]\bullet 3H_2O$, with approximately 50 mL of Sodium Hydroxide Solution II in a 100-mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II and store at ≤6 ºC in an amber reagent bottle. The solution is relatively stable and may be stored for up to one month. Bring to room temperature prior to use.

7.23 Iron Cyanide Standard Solution I (100 mg/L $[Fe(CN)_6]^{4-}$) - Dilute exactly 10 mL of $Fe(CN)_6^{4-}$ Stock Solution (Sec. 7.22) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.24 Iron Cyanide Standard Solution II (10 mg/L $[Fe(CN)_6]^{4-}$) - Dilute exactly 10 mL of $Fe(CN)_6^{4-}$ Standard Solution I (Sec. 7.23) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.25 Iron Cyanide Standard Solution III (100 µg/L $[Fe(CN)_6]^{4-}$) - Dilute exactly 1 mL of $Fe(CN)_6^{4-}$ Standard Solution II (Sec. 7.24) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.26 Nickel Cyanide Stock Solution (1000 mg/L $[Ni(CN)_4]^{2-}$) - Dissolve exactly 0.1481 + (0.0111 x *n*) g of potassium nickel cyanide mono- or polyhydrate, $K_2[Ni(CN)_4]\bullet nH_2O$ (where *n* = number of water molecules of hydration), with approximately 50 mL of Sodium Hydroxide

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Solution II in a 100-mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II and store at ≤6 ºC in an amber reagent bottle. The solution may be stored for up to two weeks. Bring to room temperature prior to use.

7.27 Nickel Cyanide Standard Solution I (100 mg/L $[Ni(CN)_4]^{2-}$) - Dilute exactly 10 mL of $[Ni(CN)_4]^{2-}$ Stock Solution (Sec. 7.26) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.28 Nickel Cyanide Standard Solution II (10 mg/L $[Ni(CN)_4]^{2-}$) - Dilute exactly 10 mL of $[Ni(CN)_4]^{2-}$ Standard Solution I (Sec. 7.27) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.29 Nickel Cyanide Standard Solution III (100 µg/L $[Ni(CN)_4]^{2-}$) - Dilute exactly 1 mL of $[Ni(CN)_4]^{2-}$ Standard Solution II (Sec. 7.28) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.30 Silver Cyanide Stock Solution(1000 mg/L $[Ag(CN)_2]^-$) - Dissolve exactly 0.1244 g of potassium silver cyanide, $K[Ag(CN)_2]$, with approximately 50 mL of Sodium Hydroxide Solution II in a 100-mL volumetric flask. Dilute to volume with Sodium Hydroxide Solution II and store at ≤6 ºC in an amber reagent bottle. The solution may be stored for up to two weeks. Bring to room temperature prior to use.

7.31 Silver Cyanide Standard Solution I (100 mg/L $[Ag(CN)_2]^-$) - Dilute exactly 10 mL of $[Ag(CN)_2]^-$ Stock Solution (Sec. 7.30) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.32 Silver Cyanide Standard Solution II (10 mg/L $[Ag(CN)_2]^-$) - Dilute exactly 10 mL of $[Ag(CN)_2]^-$ Standard Solution I (Sec. 7.31) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.33 Silver Cyanide Standard Solution III (100 µg/L $[Ag(CN)_2]^-$) - Dilute exactly 1 mL of $[Ag(CN)_2]^-$ Standard Solution II (Sec. 7.32) to 100 mL with Sodium Hydroxide Solution II. Store the solution in an amber reagent bottle. Prepare daily with analysis.

7.34 Calibration blank - Use Sodium Hydroxide Solution II (Sec. 7.8).

7.35 Iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$ - Certified ACS grade or equivalent

7.36 Helium gas - Ultra high purity

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

Sample collection, preservation and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation and storage requirements.

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8.1 Samples should 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 ≤ 300 nm in order to prevent photodecomposition of metal cyanide complexes.

8.2 Aqueous samples for complexed-metal cyanide analysis should be preserved under alkaline conditions by adjusting the pH to 12 or greater using sodium hydroxide. Solid waste samples should be stored at ≤6 ºC after collection and prior to extraction.

8.3 Store all sample matrices at ≤6 ºC for no longer than 14 days. Solid phase samples must be extracted within 14 days of sample collection. Bring the samples to room temperature prior to analysis. Analysis of aqueous samples and solid phase extract solutions must be performed within 14 days of sample collection or extract generation.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency Prior to the analysis of samples an initial demonstration of method proficiency is accomplished through the successful calibration of method-specific instruments according to project requirements and criteria set forth in the applicable analytical methodology. This initial demonstration should be performed prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure). Documentation of IDP should be maintained by the Quality Assurance Manager.

An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship may be depicted graphically, and referred to as a “calibration curve.” Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte (and surrogate for organic compounds). All reported concentrations for target analytes should be within the high and low initial calibration standards. Data generated above the high standard should be diluted into the calibration range and reanalyzed. The frequency requirements for the initial calibration vary among the individual methods.

Most analytical methods require multipoint (three or more) calibration that may include calibration blanks and higher levels so that unknowns fall within the calibration range and are bracketed by calibration points. The number of calibration points, the calibration range, and the frequency requirements should be specified in the QAPP.

If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better

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accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000D, Section 9.3 for information on how to accomplish a demonstration of proficiency.

9.3 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are free from contaminants and interferences. This is accomplished through the analysis of a method blank (See Sec. 7.9 and 9.4.1). As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source of the contamination or interference and eliminate it, if possible, before processing the samples. The method blanks should be carried through all stages of sample preparation and analysis.

The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the method blank results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.4 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample in each analytical batch. Any method blanks, matrix spike samples, and replicate samples must be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

The following should be included within each analytical batch:

9.4.1 Method blank - For each batch of solid phase samples extracted using Method 9013 (maximum 20), at least one extraction method blank should also be carried through the entire sample extraction, preparation and analytical process. An extraction method blank is prepared by using a specified volume or weight of the Method 9013 extraction solution and then carrying it through the appropriate steps of the extraction and analytical process. These steps may include, but are not limited to, prefiltering, extraction, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that exceeds the project-specific criteria requirements, then the method blank would be considered acceptable. In the absence of project-specific criteria, if the blank is less than the lower limit of detection, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank must be prepared again and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other criteria, then the data should not be rejected based on this analysis.

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9.4.2 MS/MSD - For each batch of waters processed (maximum 20), at least one analytical MS/MSD sample must be carried through the entire sample preparation and analytical process. MS/MSDs are intra-laboratory split samples spiked with identical concentrations of each analyte of interest. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. MS/MSD samples should be spiked at the same level, with the same spiking material, as that used to prepare the calibration standards and at the project-specific action level or, when lacking project-specific action levels, between the low- and mid-level standards. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of historical data this limit should be set at ±25% of the spiked concentration for accuracy and 25 relative percent difference (RPD) for precision. After the generation of historical data, 25% must still be the limit of maximum deviation for RPD to express precision and ±25% of the spiked concentration for accuracy. A separate spiked sample and a separate duplicate unspiked sample may be analyzed in lieu of MS/MSD analyses. If the bias and precision indicators are outside the laboratory control limits, or if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 25%, the interference test as discussed in Method 8000 should be conducted.

9.4.3 MS/MSD - For each batch of solid phase samples extracted using Method 9013 (maximum 20), at least one extraction MS/MSD sample should be carried through the entire sample extraction, preparation and analytical process. Spiking is performed directly on the solid sample matrix prior to extraction in order to assess the efficiency of the extraction procedure. The spiking source material should consist of a solid phase metal cyanide compound that sufficiently challenges the extraction procedure. An example of such a compound is iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$ (also known as Prussian Blue). Although insoluble under neutral and low pH conditions, $Fe_4[Fe(CN)_6]_3$ will dissolve under the alkaline extraction conditions of Method 9013 and quantitatively yield $[Fe(CN)_6]^{4-}$ in the extraction solution, which can subsequently be analyzed in order to verify extraction efficiency. Other metal cyanide compounds may be used for spiking the solid sample matrix, depending on which aqueous metal cyanide complexes are of greatest interest in the analysis. Refer to the guidance given Sec. 9.5.3 for accuracy and precision acceptance criteria for the extraction MS/MSD.

9.4.5 LCS - For each batch of samples processed (maximum 20), at least one LCS must be carried through the entire sample preparation and analytical process, as described in Chapter One. The LCS is a reagent water solution fortified with method analytes at known concentrations, prepared from a different source than that used to prepare the calibration standards. The LCS should be spiked with each analyte of interest at the project-specific action level or when lacking project-specific action levels, between the low- and mid-level standards. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ±20% of the spiked concentration. After the generation of historical data, ±20% must still be the acceptable limit of maximum deviation. If the LCS recovery is not acceptable, the LCS should be re-run once and, if still unacceptable, all samples after the last acceptable LCS must be prepared again and reanalyzed. Concurrent analyses of standard reference materials (SRMs) containing known values of analytes in the media of interest are recommended and may be used as an LCS.

9.4.6 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.5 Initial Calibration Verification (ICV)

Immediately after the calibration standards have been analyzed, the accuracy of the calibration must be verified by the analysis of an ICV standard. The ICV is prepared in the same manner as a calibration standard at a concentration level within the calibration range of the method and using a second source standard (prepared using standards different from the calibration standards) spiked into Sodium Hydroxide Solution II (see Sec. 7.8). The control limit for the ICV is ±15% of the true value. When the ICV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.6 Continuing Calibration Verification (CCV)

Once the calibration curve has been established, the continuing accuracy must be verified by analysis of a CCV after every tenth field sample, and at the end of the analysis sequence. The CCV is equivalent to or prepared in the same manner as a calibration standard at a concentration level within the calibration range of the method and using the same source standard (prepared using the same source standards as those used to prepare the calibration standards) spiked into Sodium Hydroxide Solution II (see Sec. 7.8). CCV concentrations alternating between the low- and mid-range calibration standard concentrations are recommended. The control limit for the low-range CCV is ± 50% and for the mid-range CCV is ± 15% of the true value. When the CCV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified using an ICV analysis. Samples that are not bracketed by acceptable CCV runs must be reanalyzed.

9.7 Lower Limit of Quantitation (LLOQ) check standard

The laboratory should establish the LLOQ as the lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. The LLOQ verification is recommended for each project application to validate quantitation capability at low analyte concentration levels. This verification may be accomplished either with clean control material (e.g., reagent water, method blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix (free of target compounds). Optimally, the LLOQ should be less than or equal to the desired regulatory action levels based on the stated project-specific requirements. The LLOQ should be verified by the analysis of at least 7 replicate samples, spiked at the LLOQ and processed through all preparation and analysis steps of the method. The mean recovery and relative standard deviation of these samples provide an initial statement of precision and accuracy at the LLOQ. In most cases the mean recovery should be +/- 35% of the true value and RSD should be < 20%. In-house limits may be calculated when sufficient data points exist.

9.7.1 The determination of LLOQs using spiked clean control material represents a best-case scenario, and does not evaluate the potential matrix effects of real-world samples. For the application of LLOQs on a project-specific basis, with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

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9.7.1.1 A matrix-free LLOQ check standard is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). This LLOQ check is carried through the same preparation procedures as the environmental samples and other QC. Recovery should be ±50% (or other such project-required acceptance limits for accuracy and precision) of the true value to verify the data reporting limits(s). The low-range CCV standard (Sec. 9.6), if prepared at the appropriate concentration, may also serve as the LLOQ verification for confirming method sensitivity.

9.7.1.2 Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LLOQ concentration levels. This LLOQ check is carried through the same preparation procedures as the environmental samples and other QC. Individual LLOQs are verified when each respective analyte is recovered at ±50% of the predicted LLOQ concentration or established DQO criteria. This check may also be applied towards establishing the individual analyte reporting limit(s).

9.7.2 In-house limits may be calculated when sufficient data points exist.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration standards - Prepare calibration standards so as to bracket the ranges of each metal cyanide complex of interest by adding measured volumes of metal cyanide standards (Sec. 7.0) to volumetric flasks and diluting to volume. Approximate calibration ranges for each metal cyanide complex are provided in Tables 1 and 2. Dilute the standards to their respective final volumes using Sodium Hydroxide Solution II (Sec. 7.8). Prepare at least three standards or as otherwise required for data reporting. Store the standards in amber bottles.

10.2 To establish the calibration curve, analyze the calibration blank (Sec. 7.34) and calibration standards in accordance with the procedure in Sec. 11.0. Plot calibration curves of peak area response verses analyte concentration for each metal cyanide using the method blank peak area integration for the zero point. Perform linear regressions of the plots. A second order regression plot may be used if needed. The correlation coefficient of each regression should be 0.995 or greater for accurate results. 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 Sec. 9.0.

NOTE: Since all iron cyanide species are detected as ferrocyanide, that form of iron cyanide is used in the preparation of the calibration standards. The calibration and subsequent analysis results for iron cyanide should be presented as either $[Fe(CN)_6]^{x-}$ or $[Fe(CN)_6]^{3-/4-}$ so as to represent the total sum of ferrocyanide and ferricyanide.

11.0 PROCEDURE

11.1 For aqueous samples, proceed to Sec. 11.3 or 11.4.

11.2 For solid waste extract solutions to be analyzed by this method, the following steps need to be performed after the Method 9013 extraction process:

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11.2.1 Following the 16 hour extraction, check the pH of the extraction solution. Adjust the pH between 11 and 12, using 50% H_2SO_4. Recap the extraction flask and mix the solution. Repeat the procedure until the pH is in the desired range.

11.2.2 Prepare a Buchner funnel apparatus with a 0.45-μm membrane filter.

11.2.3 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

11.2.4 If not analyzed immediately, transfer the extract into a dark plastic/glass bottle with no headspace and store it at ≤6 ºC. Analyze the extract within 14 days.

11.3 Anion exchange chromatography analysis - Analyze samples containing 0.2-200 mg/L metal cyanide complexes by direct injection of sample or extract. Higher sample concentrations may be analyzed after an appropriate dilution.

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

11.4 Anion exchange chromatography analysis using on-line sample preconcentration - Analyze samples containing 0.5 - 200 µg/L metal cyanide complexes using on-line sample preconcentration prior to anion exchange chromatography analysis.

11.4.1 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 Figures 4 and 5.

11.4.2 Condition the MFCs according to the manufacturer's instructions and install as shown in Figure 4.

11.4.3 Set the sample concentrator pump to achieve a flow rate of 2 mL/min.

11.4.4 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 in a safe manner (see Sec. 5.0.).

11.5 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 Tables 4 and 5. Portions of the analysis program may be modified as appropriate provided the analytical results fall within the precision and bias established for the method (see Sec. 13.0.).

11.6 Install the ATC.

11.6.1 Condition the ATC according to the manufacturer's instructions.

11.6.2 Set the gradient pump to 100% Eluent 1 and prime the gradient pump line to remove trapped air.

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11.6.3 After priming, connect the conditioned ATC directly to the outlet of the gradient pump and plumb the ATC outlet line to an appropriate waste container. Pump Eluent 1 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 ATC from the outlet of the gradient pump. Dispose of the contents of the waste container as hazardous waste.

11.6.4 Place the prepared ATC between the Eluent 1 reservoir and the gradient pump inlet as shown in Figures 3 and 4 and reconnect the gradient pump outlet line to the injection valve.

NOTE: The ATC is capable of treating only a limited amount of Eluent 1. For optimum performance, the column must be replaced or reconditioned following treatment of each 2-3 L of Eluent 1.

11.7 Prime the gradient pump lines for Eluents 1, 2 and 3 separately to remove trapped air within each line. To do this, select one eluent, set to 100%, and begin priming. Repeat this step for the remaining eluents.

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

11.9 Connect the guard and analytical columns in 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.

11.10 Allow the instrument to equilibrate 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.

11.11 Set the UV/Vis detector to 215 nm and offset the absorbance to zero.

NOTE: Eluent is pumped through the concentrator column by placing the injection valve in the "Inject" mode (See Figure 5.).

11.12 Check the sample pH and adjust, if needed, to pH 11-12 using 50% H_2SO_4.

11.13 Filter an appropriate volume of aqueous sample using a plastic syringe fitted with a 0.45-μm syringe filter. Alternatively, use a portion of filtered extract obtained from the alkaline extraction procedure (e.g., Method 9013).

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

11.15 Transfer the method blank, calibration blank, calibration standards and QA/QC samples (see Sec. 9.0.) and standards to amber sample vials.

11.16 Place all of the vials in the autosampler.

11.17 Start the autosampler, and instrument control and data collection system, and begin analyzing the samples. A water blank should be analyzed first to equilibrate the columns followed by the method blank, calibration standards (Sec. 10.1) and samples, including QC

samples (Sec. 9.0). Use an injection volume of approximately 0.1 mL for samples containing 0.2 - 200 mg/L metal cyanide complexes and an injection volume of approximately 5 - 20 mL when using sample preconcentration for samples containing 0.5-200 μg/L metal cyanide complexes. Periodically and after the analysis of no more than 20 samples, analyze a continuing calibration verification standard to assess instrument drift throughout the run (See Sec. 9.6). Examples of method chromatograms are provided in Figures 6 through 11.

11.18 Confirmation

Tentative identification of the analyte occurs when a peak from the sample falls within the retention time window established by the calibration standards. Confirmation is recommended when the sample composition is not well characterized. Confirmatory techniques such as anion exchange chromatography with a dissimilar column or anion exchange chromatography with a dissimilar detection method such as inductively coupled plasma-mass spectrometry (ICP-MS) can be used.

When analyte identification is successfully confirmed using two dissimilar columns or two dissimilar detectors, the disparity between the quantitative results should be formally evaluated by determining the RPD. The RPD acceptance criteria and data reporting requirements should be established based on the intended application of the data. See Method 8000, Sec. 11 (Ref. 19) for additional guidance.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Derive the concentration of each respective metal cyanide analyte in either mg/L or μg/L in the samples using the regression plot as described in Sec. 10.2. Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

12.2 Use the following calculation to convert sample concentrations expressed as mg/L to mg/kg for a solid waste matrix:

$$\frac{\text{mg}}{\text{kg}}\left[\text{M}(\text{CN})_b\right]^{x-} = \frac{\text{mg}}{\text{L}}\left[\text{M}(\text{CN})_b\right]^{x-} \times \frac{\text{L extraction volume}}{\text{g sample}} \times \frac{1000\ \text{g}}{\text{kg}}$$

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

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

The formula weights for cyanide as well as those for each of the metal cyanide complexes are provided in Table 6.

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13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Tables 7 through 12 present precision and bias data from multiple laboratories for a spiked reagent water, groundwater and soil extract using anion exchange chromatography. These data are provided for guidance purposes only.

13.3 Tables 13 through 18 present precision and bias data from multiple laboratories for a spiked reagent water, groundwater and soil extract using anion exchange chromatography equipped with on-line sample preconcentration. These data are provided for guidance purposes only.

13.4 Table 19 presents total cyanide extraction recoveries for spiked solid waste samples prepared using Method 9013. These data are provided for guidance purposes only.

13.5 A lack of significant analytical bias has been confirmed by comparing the results of the test method to those obtained using anion exchange chromatography coupled with ICP-MS detection for a variety of environmental matrices. (See Ref. 1.)

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction,* a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety.
http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the ACS publication listed in Sec. 14.2.

15.2 Some of the reagents and solutions used in this method as well as the effluent from the chromatograph contain cyanide and should be handled and disposed of in an approved manner.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The pages to follow contain the tables and figures referenced by this method.

TABLE 1

APPROXIMATE CALIBRATION RANGES FOR METAL CYANIDE COMPLEXES
DETERMINED BY ANION EXCHANGE CHROMATOGRAPHY

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

Data taken from Reference 1.

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TABLE 2

APPROXIMATE CALIBRATION RANGES FOR METAL CYANIDE COMPLEXES DETERMINED BY ANION EXCHANGE CHROMATOGRAPHY USING ON-LINE SAMPLE PRECONCENTRATION

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

Data taken from Reference 1.

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TABLE 3

STABILITY CONSTANTS OF METAL CYANIDE COMPLEXES

Metal Cyanide Complex	Stability Constant (log K at 25ºC, I[a] = 0.0)
$[Ag(CN)_2]^-$	20.5
$[Co(CN)_6]^{3-}$	64.0[b]
$[Ni(CN)_4]^{2-}$	30.2
$[Cu(CN)_4]^{3-}$	30.3
$[Fe(CN)_6]^{4-}$	35.4
$[Au(CN)_2]^-$	126[c]

[a] I = Ionic Strength
[b] The stability constant is considered to be an estimate
[c] For the reaction: $[AuO_3]^{3-} + 2CN^- + 6H^+ + 2e^- \rightarrow [Au(CN)_2]^- + 3H_2O$

Data taken from References 20 and 21.

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TABLE 4

METHOD SETTINGS FOR THE ANALYSIS OF METAL CYANIDE COMPLEXES USING GRADIENT ELUTION

Time (min)	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.

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TABLE 5

METHOD SETTINGS FOR THE ANALYSIS OF METAL CYANIDE COMPLEXES USING GRADIENT ELUTION AND ON-LINE SAMPLE PRECONCENTRATION

	Two-way Switching Valve	Gradient Pump				Absorbance Detector		Sample Concentrator Pump	Comments and Function
Time (min)	Position	Flow Rate (mL/min)	Eluent 1 (%)	Eluent 2 (%)	Pump 3 (%)	Wavelength (nm)	Data Collection (Absorbance Units)	(2 mL/min)	
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.

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TABLE 6

CYANIDE SPECIES FORMULA WEIGHTS

Cyanide Species	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

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TABLE 7

EXAMPLE $[Fe(CN)_6]^{4-}$ ANALYSIS PRECISION AND BIAS
USING ANION EXCHANGE CHROMATOGRAPHY

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (mg/L)	S_T (mg/L)	Bias
Reagent Water	1.0	1.08	7			0.06	8.4%
	1.2	1.30	6	6	0.03	0.03	8.2%
	9.0	9.48	6			0.10	5.3%
	10.0	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%
Groundwater	1.0	1.05	7			0.02	4.7%
	1.2	1.28	7	7	0.02	0.04	6.4%
	9.0	9.42	6			0.09	4.6%
	10.0	10.51	7	6	0.07	0.24	5.1%
	17.5	18.29	7			0.42	4.5%
	18.5	19.28	7	7	0.07	0.36	4.2%
Soil Extract	1.0	1.09	3			0.08	8.7%
	1.2	1.25	3	3	0.03	0.04	4.3%
	9.0	9.36	3			0.14	4.0%
	10.0	10.32	3	3	0.05	0.08	3.2%
	17.5	18.06	3			0.16	3.2%
	18.5	19.22	3	3	0.10	0.13	3.9%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 8

EXAMPLE $[Cu(CN)_3]^{2-}$ ANALYSIS PRECISION AND BIAS
USING ANION EXCHANGE CHROMATOGRAPHY

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (mg/L)	S_T (mg/L)	Bias
Reagent Water	0.20	0.22	7			0.02	10.0%
	0.24	0.30	6	6	0.01	0.01	23.9%
	0.90	0.97	6			0.06	7.3%
	1.0	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%
Groundwater	0.20	0.22	7			0.01	7.9%
	0.24	0.30	7	7	0.01	0.02	22.7%
	0.90	0.96	6			0.04	6.9%
	1.0	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%
Soil Extract	0.20	0.23	3			0.02	16.2%
	0.24	0.26	3	3	0.01	0.01	7.2%
	0.85	0.94	3			0.04	10.9%
	0.95	1.00	3	3	0.01	0.03	5.1%
	1.6	1.70	3			0.07	6.3%
	1.7	1.80	3	3	0.01	0.09	6.1%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 9

EXAMPLE $[Ag(CN)_2]^-$ ANALYSIS PRECISION AND BIAS
USING ANION EXCHANGE CHROMATOGRAPHY

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (mg/L)	S_T (mg/L)	Bias
Reagent Water	21.0	22.94	7			1.22	9.2%
	23.0	25.31	7	7	0.59	1.09	10.1%
	46.0	50.13	6			1.80	9.0%
	51.0	55.46	7	6	0.49	1.56	8.7%
	85.0	88.36	7			1.61	3.9%
	90.0	94.00	7	7	1.42	1.82	4.4%
Groundwater	21.0	23.68	7			0.54	12.8%
	23.0	25.90	7	7	0.84	0.92	12.6%
	46.0	50.86	7			1.47	10.6%
	51.0	55.86	7	7	0.47	1.11	9.5%
	85.0	90.37	7			2.20	6.3%
	90.0	94.77	7	7	0.45	2.08	5.3%
Soil Extract	21.0	22.47	3			0.37	7.0%
	23.0	24.17	3	3	0.17	0.34	5.1%
	46.0	48.45	3			0.77	5.3%
	51.0	53.06	3	3	0.22	0.50	4.0%
	85.0	88.58	3			0.46	4.2%
	90.0	92.38	3	3	1.58	1.85	2.6%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 10

EXAMPLE $[Au(CN)_2]^-$ ANALYSIS PRECISION AND BIAS
USING ANION EXCHANGE CHROMATOGRAPHY

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (mg/L)	S_T (mg/L)	Bias
Reagent Water	10.0	10.98	7			0.64	9.8%
	12.0	12.59	6	6	0.40	0.26	4.9%
	20.0	22.00	7			1.97	10.0%
	22.0	23.09	6	6	1.34	0.58	5.0%
	40.0	41.57	6			0.86	3.9%
	42.0	43.29	6	6	0.47	0.93	3.1%
Groundwater	10.0	10.53	6			0.41	5.3%
	12.0	12.38	7	6	0.43	0.69	3.1%
	20.0	21.56	7			1.13	7.8%
	22.0	22.73	7	7	1.43	1.26	3.3%
	40.0	42.27	6			0.83	5.7%
	42.0	44.00	6	6	0.55	0.81	4.8%
Soil Extract	10.0	10.35	3			0.37	3.5%
	12.0	11.75	3	3	0.61	1.04	-2.1%
	20.0	20.44	3			0.68	2.2%
	22.0	22.62	3	3	0.16	0.65	2.8%
	40.0	41.82	3			0.61	4.6%
	42.0	44.12	3	3	0.60	1.12	5.1%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 11

EXAMPLE $[Co(CN)_6]^{3-}$ ANALYSIS PRECISION AND BIAS
USING ANION EXCHANGE CHROMATOGRAPHY

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (mg/L)	S_T (mg/L)	Bias
Reagent Water	15.0	15.63	7			0.39	15.0
	18.0	18.67	7	7	0.23	0.40	18.0
	46.0	47.78	6			0.40	46.0
	50.0	51.42	6	6	0.25	0.14	50.0
	85.0	86.17	7			0.66	85.0
	90.0	91.01	7	7	0.68	1.52	90.0
Groundwater	15.0	15.71	7			0.48	4.7%
	18.0	18.83	7	7	0.18	0.32	4.6%
	46.0	47.87	7			0.91	4.1%
	50.0	51.31	7	7	0.27	1.12	2.6%
	85.0	86.48	7			1.75	1.7%
	90.0	91.35	7	7	0.21	1.93	1.5%
Soil Extract	15.0	15.64	3			0.43	4.2%
	18.0	18.53	3	3	0.07	0.51	3.0%
	46.0	47.43	3			1.24	3.1%
	50.0	50.96	3	3	0.34	1.08	1.9%
	85.0	86.16	3			2.41	1.4%
	90.0	91.55	3	3	0.25	2.18	1.7%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 12

EXAMPLE $[Ni(CN)_4]^{2-}$ ANALYSIS PRECISION AND BIAS
USING ANION EXCHANGE CHROMATOGRAPHY

Matrix	Amount Added (mg/L)	Amount Found (mg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (mg/L)	S_T (mg/L)	Bias
Reagent Water	20.0	21.93	7			0.98	9.6%
	24.0	25.91	7	7	0.48	1.18	7.9%
	85.0	91.15	7			2.10	7.2%
	95.0	101.6	7	7	0.72	2.40	6.9%
	175	185.9	7			9.64	6.2%
	185	193.5	7	7	2.33	8.65	4.6%
Groundwater	20.0	21.62	7			1.67	8.1%
	24.0	25.47	7	7	0.43	1.74	6.1%
	85.0	90.49	6			1.05	6.5%
	95.0	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%
Soil Extract	20.0	21.29	3			0.27	8.4%
	24.0	26.00	3	3	0.07	2.27	4.7%
	85.0	89.02	3			1.97	5.6%
	95.0	100.35	3	3	0.53	5.10	2.6%
	175	179.47	3			6.31	3.1%
	185	190.82	3	3	1.54	0.00	0.0%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 13

EXAMPLE $[Fe(CN)_6]^{4-}$ ANALYSIS PRECISION AND BIAS USING ANION EXCHANGE CHROMATOGRAPHY AND ON-LINE SAMPLE PRECONCENTRATION

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Retained 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%
	11.0	10.90	6	6	0.38	0.41	-1.0%
	17.0	16.53	6			1.16	-2.8%
	18.0	17.49	6	6	1.06	0.88	-2.9%
Groundwater	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%
	11.0	10.94	5	5	0.30	0.50	-0.5%
	17.0	17.53	5			0.98	3.1%
	18.0	18.08	5	5	0.92	0.46	0.4%
Soil Extract	1.6	1.75	1				9.5%
	1.8	1.98	1	1	NA	NA	10.1%
	9.5	9.72	1				2.3%
	11.0	11.21	1	1	NA	NA	2.0%
	17.0	17.66	1				3.9%
	18.0	18.57	1	1	NA	NA	3.2%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories
NA = Not Applicable, single laboratory study

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 14

EXAMPLE $[Cu(CN)_3]^{2-}$ ANALYSIS PRECISION AND BIAS USING ANION EXCHANGE CHROMATOGRAPHY AND ON-LINE SAMPLE PRECONCENTRATION

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Retained 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%
Groundwater	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%
Soil Extract	1.1	0.32	1				-71.0%
	1.3	0.32	1	1	NA	NA	-75.5%
	2.3	0.51	1				-78.0%
	2.5	0.84	1	1	NA	NA	-66.3%
	4.4	1.00	1				-77.3%
	4.6	1.06	1	1	NA	NA	-76.9%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories
NA = Not Applicable, single laboratory study

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 15

EXAMPLE $[Ag(CN)_2]^-$ ANALYSIS PRECISION AND BIAS USING ANION EXCHANGE CHROMATOGRAPHY AND ON-LINE SAMPLE PRECONCENTRATION

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (µg/L)	S_T (µg/L)	Bias
Reagent Water	20.0	25.05	6			8.62	25.2%
	24.0	28.64	6	6	1.57	8.12	19.3%
	50.0	49.57	6			10.15	-0.9%
	54.0	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%
Groundwater	20.0	10.19	5			1.77	-49.1%
	24.0	15.45	6	5	1.12	4.38	-35.6%
	50.0	29.11	6			5.94	-41.8%
	54.0	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%
Soil Extract	20.0	15.27	1				-23.6%
	24.0	18.11	1	1	NA	NA	-24.6%
	50.0	52.56	1				5.1%
	54.0	57.99	1	1	NA	NA	7.4%
	110.0	117.32	1				6.7%
	115.0	122.13	1	1	NA	NA	6.2%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories
NA = Not Applicable, single laboratory study

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 16

EXAMPLE $[Au(CN)_2]^-$ ANALYSIS PRECISION AND BIAS USING ANION EXCHANGE CHROMATOGRAPHY AND ON-LINE SAMPLE PRECONCENTRATION

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (µg/L)	S_T (µg/L)	Bias
Reagent Water	15.0	16.47	6			1.14	9.8%
	18.0	18.46	6	6	0.98	1.37	2.5%
	57.0	58.49	6			3.91	2.6%
	60.0	64.07	6	6	3.00	4.11	6.8%
	85.0	87.04	5			0.63	2.4%
	90.0	90.10	6	5	1.58	4.81	0.1%
Groundwater	15.0	14.25	6			1.49	-5.0%
	18.0	17.14	5	5	0.77	2.28	-4.8%
	57.0	53.66	6			5.58	-5.9%
	60.0	56.16	6	6	4.12	6.63	-6.4%
	85.0	82.05	6			4.72	-3.5%
	90.0	84.58	6	6	2.75	8.31	-6.0%
Soil Extract	15.0	15.95	1				6.3%
	18.0	18.10	1	1	NA	NA	0.5%
	57.0	60.63	1				6.4%
	60.0	62.64	1	1	NA	NA	4.4%
	85.0	87.57	1				3.0%
	90.0	95.84	1	1	NA	NA	6.5%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories
NA = Not Applicable, single laboratory study

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 17

EXAMPLE $[Co(CN)_6]^{3-}$ ANALYSIS PRECISION AND BIAS USING ANION EXCHANGE CHROMATOGRAPHY AND ON-LINE SAMPLE PRECONCENTRATION

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (µg/L)	S_T (µg/L)	Bias
Reagent Water	12.0	12.46	7			0.88	3.9%
	14.0	14.05	7	7	0.45	1.44	0.3%
	95.0	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%
Groundwater	12.0	12.96	6			1.49	8.0%
	14.0	14.67	5	5	0.34	1.61	4.8%
	95.0	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%
Soil Extract	12.0	11.38	1				-5.1%
	14.0	13.47	1	1	NA	NA	-3.8%
	95.0	100.30	1				5.6%
	105.0	109.09	1	1	NA	NA	3.9%
	180.0	188.41	1				4.7%
	190.0	198.35	1	1	NA	NA	4.4%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories
NA = Not Applicable, single laboratory study

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 18

EXAMPLE $[Ni(CN)_4]^{2-}$ ANALYSIS PRECISION AND BIAS USING ANION EXCHANGE CHROMATOGRAPHY AND ON-LINE SAMPLE PRECONCENTRATION

Matrix	Amount Added (µg/L)	Amount Found (µg/L)	Number of Retained Samples	Number of Retained Youden Pairs	S_O (µg/L)	S_T (µg/L)	Bias
Reagent Water	55.0	53.52	5			1.21	-2.7%
	60.0	59.31	6	5	2.53	3.98	-1.1%
	75.0	73.54	6			5.56	-2.0%
	80.0	78.47	5	5	3.25	1.32	-1.9%
	90.0	90.75	6			5.79	0.8%
	95.0	95.72	6	6	5.50	6.86	0.8%
Groundwater	55.0	43.32	6			9.97	-21.2%
	60.0	39.20	6	6	15.25	19.34	-34.7%
	75.0	55.89	6			8.81	-25.5%
	80.0	59.92	6	6	2.93	6.57	-25.1%
	90.0	71.95	6			10.24	-20.1%
	95.0	79.89	6	6	9.42	12.41	-15.9%
Soil Extract	55.0	50.58	1				-8.0%
	60.0	55.17	1	1	NA	NA	-8.1%
	75.0	72.77	1				-3.0%
	80.0	76.02	1	1	NA	NA	-5.0%
	90.0	87.76	1				-2.5%
	95.0	91.23	1	1	NA	NA	-4.0%

S_T = Overall standard deviation across multiple laboratories
S_O = Single operator standard deviation across multiple laboratories
NA = Not Applicable, single laboratory study

These data are provided for guidance purposes only.

Data taken from References 1 and 22.

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TABLE 19

TOTAL CYANIDE RECOVERIES IN SPIKED SOILS PREPARED USING METHOD 9013 EXTRACTION

Sample	Background Total Cyanide Concentration[a] (µg/g Cyanide)	Spiking Concentration[b] (µg/g Cyanide)	Average Total Cyanide Recovery[b]	Standard Deviation[c]
Soil 1	0.44	500	95%	1.8% (n = 2)
Soil 2	0.17	500	78%	0.1% (n = 2)
Soil 3	ND	500	86%	6.4% (n = 4)

[a] Total cyanide was determined in the soil extraction solutions using EPA SW-846 Methods 9010 and 9012 (Ref. 23).

[b] Soils were spiked using solid $Fe_4[Fe(CN)_6]_3$ prior to extraction.

[c] n = Number of replicate analyses

These data are provided for guidance purposes only.

Data taken from Reference 22.

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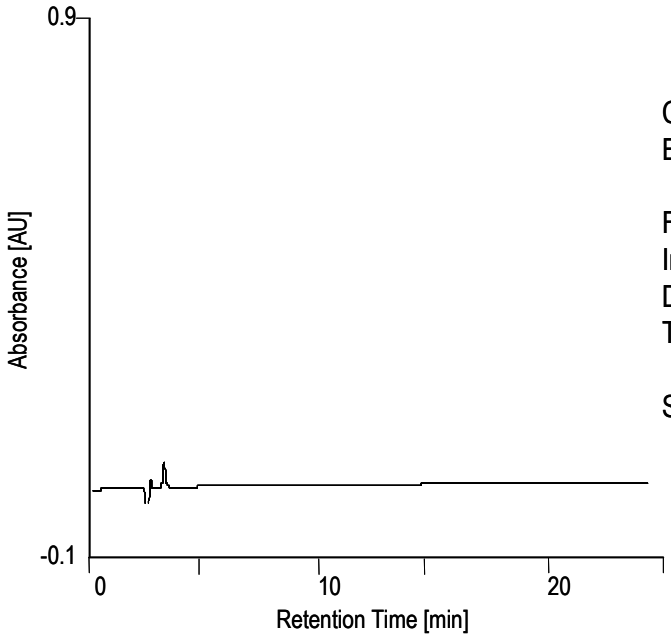
FIGURE 1

EXAMPLE BLANK REAGENT WATER CHROMATOGRAM



Column:	IonPac® AS11 (4-mm)
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN
Flow Rate:	1 mL/min
Inj. Volume:	100 µL
Detection:	Absorbance at 215 nm
Temperature:	ambient
Sample:	Reagent Water

These data are provided for guidance purposes only.

Figure taken from Reference 1.

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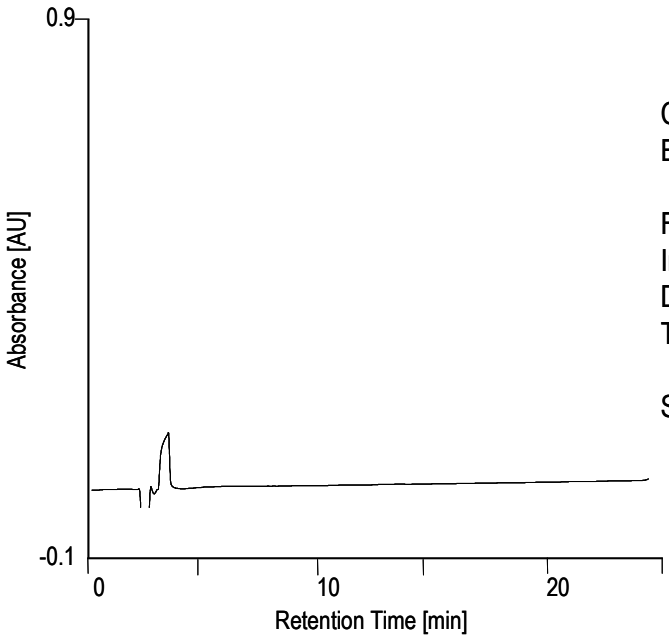
FIGURE 2

EXAMPLE BLANK REAGENT CHROMATOGRAM WATER USING
ON-LINE SAMPLE PRECONCENTRATION



Column:	IonPac® AS11 (4-mm)
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN
Flow Rate:	1 mL/min
Inj. Volume:	100 µL
Detection:	Absorbance at 215 nm
Temperature:	ambient
Sample:	Reagent Water

These data are provided for guidance purposes only.

Figure taken from Reference 1.

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FIGURE 3

CHROMATOGRAPH CONFIGURATION FOR THE ANALYSIS OF METAL CYANIDE COMPLEXES

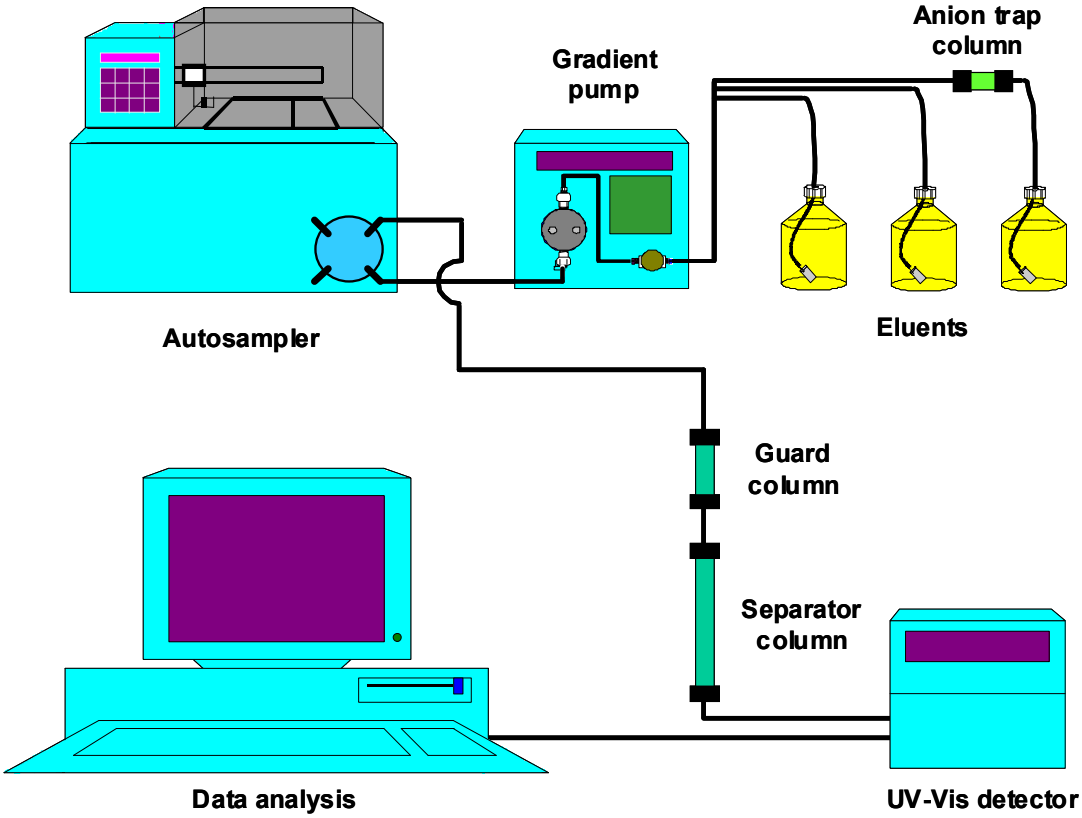

Figure taken from Reference 1.

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FIGURE 4

CHROMATOGRAPH CONFIGURATION FOR THE ANALYSIS OF METAL CYANIDE COMPLEXES USING SAMPLE PRECONCENTRATION

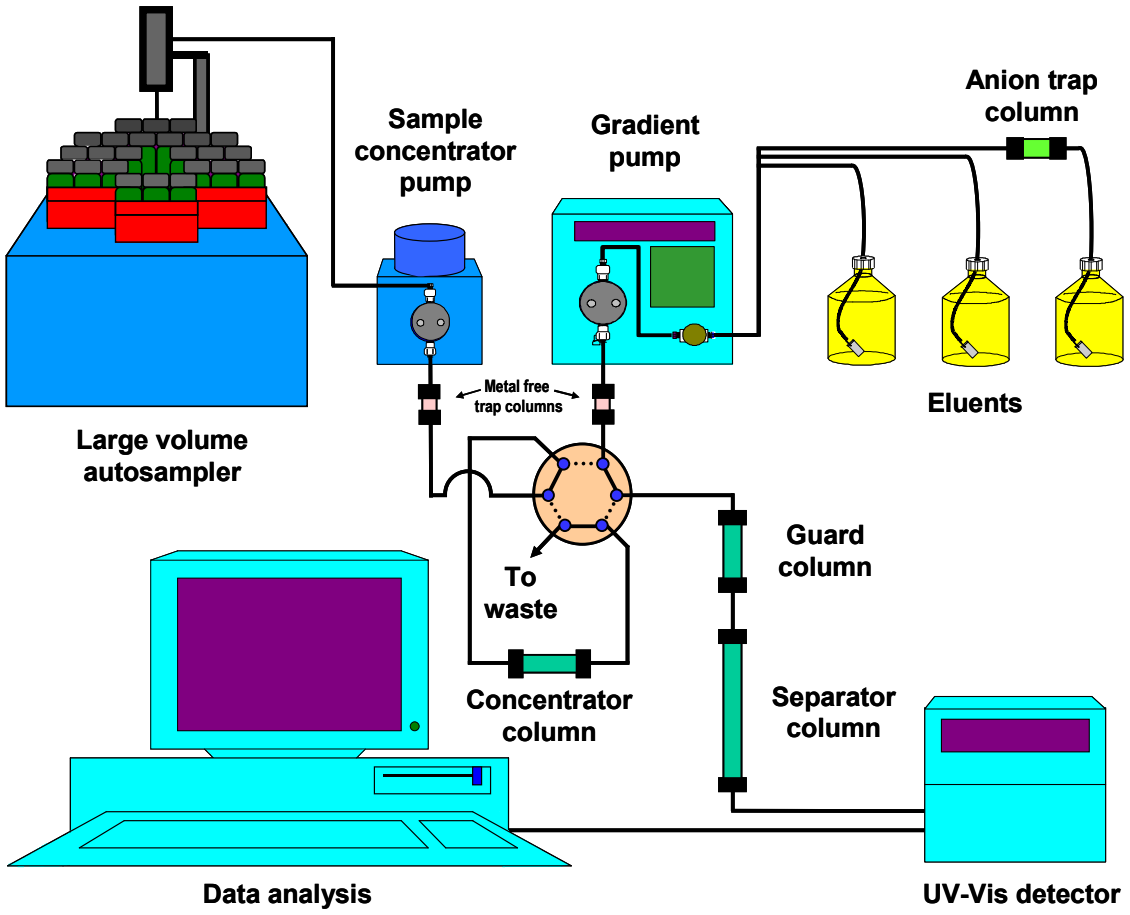

Figure taken from Reference 1.

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FIGURE 5

INJECTION VALVE CONFIGURATION FOR SAMPLE PRECONCENTRATION

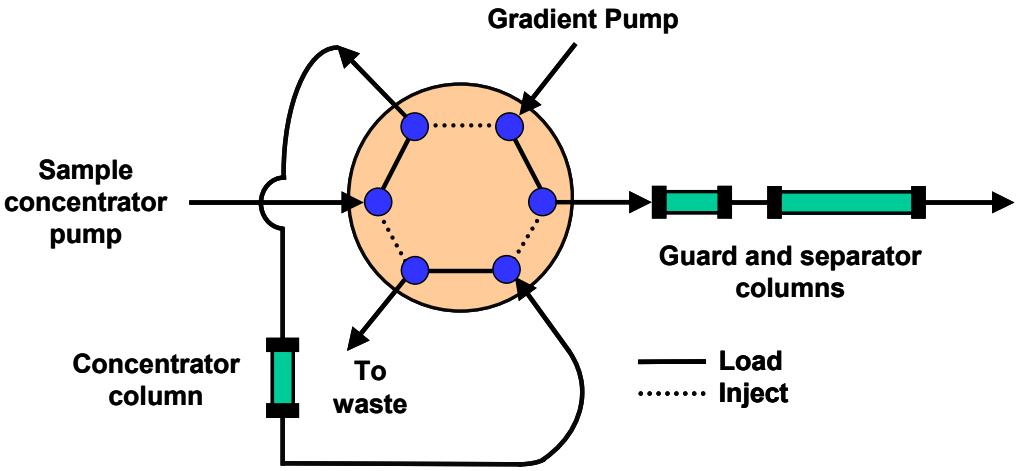

Figure taken from Reference 1.

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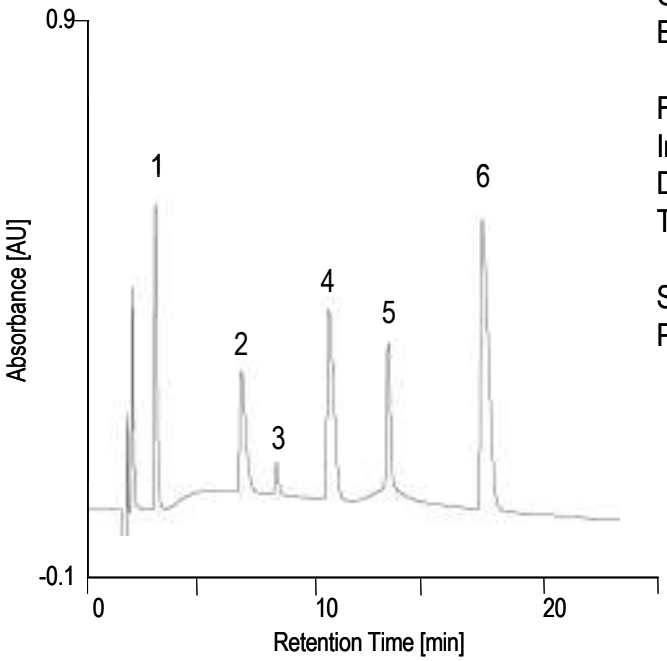
FIGURE 6

EXAMPLE SPIKED REAGENT WATER CHROMATOGRAM



Column:	IonPac® AS5 (4-mm)	
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN	
Flow Rate:	1 mL/min	
Inj. Volume:	100 µL	
Detection:	Absorbance at 215 nm	
Temperature:	ambient	
Sample:	Spiked Reagent Water	
Peaks:	1. $[Ag(CN)_2]^-$	22 mg/L
	2. $[Au(CN)_2]^-$	11
	3. $[Cu(CN)_3]^{2-}$	0.25
	4. $[Ni(CN)_4]^{2-}$	22
	5. $[Fe(CN)_6]^{4-}$	1.1
	6. $[Co(CN)_6]^{3-}$	17

These data are provided for guidance purposes only.

Figure taken from Reference 22.

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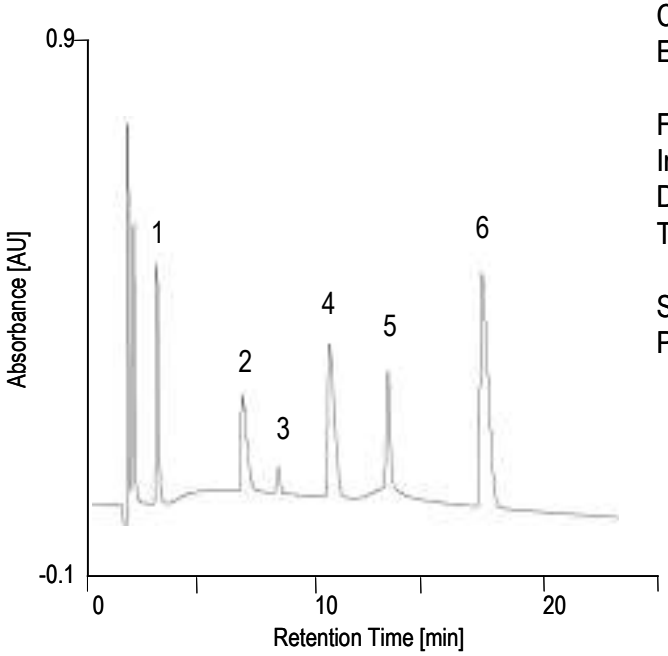
FIGURE 7

EXAMPLE SPIKED GROUNDWATER CHROMATOGRAM



Column:	IonPac® AS5 (4-mm)
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN
Flow Rate:	1 mL/min
Inj. Volume:	100 µL
Detection:	Absorbance at 215 nm
Temperature:	ambient

Sample:	Spiked Groundwater	
Peaks:	1. $[Ag(CN)_2]^-$	22 mg/L
	2. $[Au(CN)_2]^-$	11
	3. $[Cu(CN)_3]^{2-}$	0.25
	4. $[Ni(CN)_4]^{2-}$	22
	5. $[Fe(CN)_6]^{4-}$	1.1
	6. $[Co(CN)_6]^{3-}$	17

These data are provided for guidance purposes only.

Figure taken from Reference 1.

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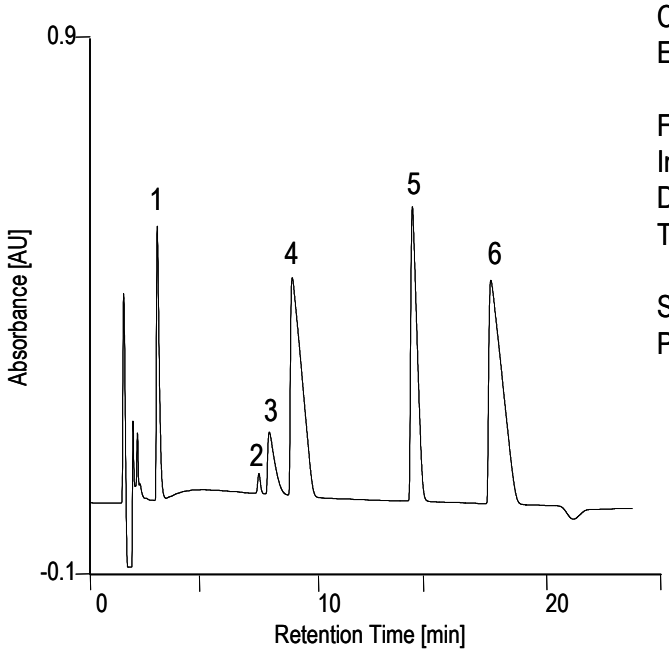
FIGURE 8

EXAMPLE SPIKED SOIL EXTRACT CHROMATOGRAM



Column:	IonPac® AS11 (4-mm)	
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN	
Flow Rate:	1 mL/min	
Inj. Volume:	100 µL	
Detection:	Absorbance at 215 nm	
Temperature:	35 °C	
Sample:	Spiked Soil Extract	
Peaks:	1. $[Ag(CN)_2]^-$	75 mg/L
	2. $[Cu(CN)_3]^{2-}$	0.5
	3. $[Au(CN)_2]^-$	25
	4. $[Ni(CN)_4]^{2-}$	150
	5. $[Fe(CN)_6]^{4-}$	15
	6. $[Co(CN)_6]^{3-}$	75

These data are provided for guidance purposes only.

Figure taken from Reference 22.

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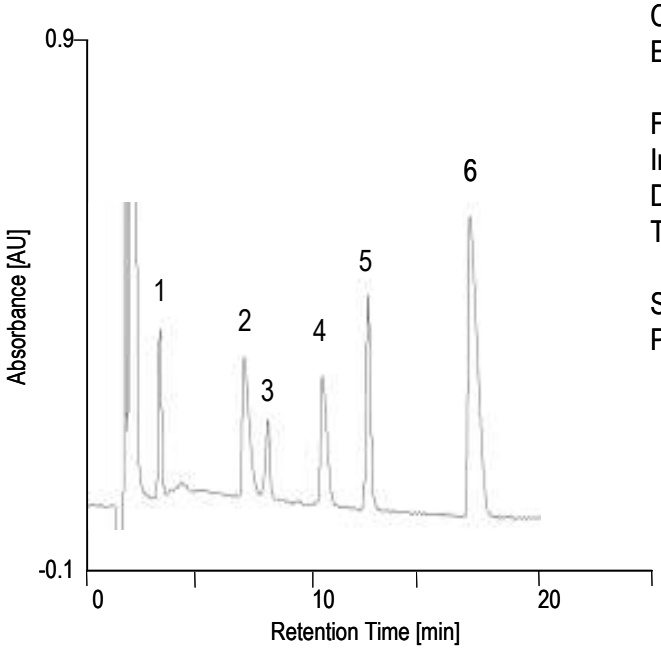
FIGURE 9

EXAMPLE SPIKED REAGENT WATER CHROMATOGRAM USING SAMPLE PRECONCENTRATION



Column:	IonPac® AS5 (4-mm)	
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN	
Flow Rate:	1 mL/min	
Inj. Volume:	20 mL concentrated on AG5	
Detection:	Absorbance at 215 nm	
Temperature:	ambient	
Sample:	Spiked Reagent Water	
Peaks:	1. $[Ag(CN)_2]^-$	100 µg/L
	2. $[Au(CN)_2]^-$	75
	3. $[Cu(CN)_3]^{2-}$	4
	4. $[Ni(CN)_4]^{2-}$	75
	5. $[Fe(CN)_6]^{4-}$	10
	6. $[Co(CN)_6]^{3-}$	100

These data are provided for guidance purposes only.

Figure taken from Reference 22.

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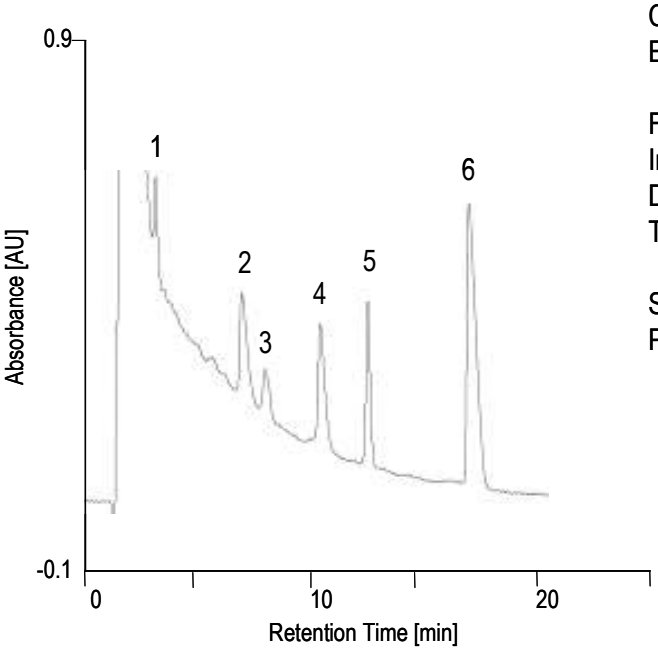
FIGURE 10

EXAMPLE SPIKED GROUNDWATER CHROMATOGRAM USING SAMPLE PRECONCENTRATION



Column:	IonPac® AS5 (4-mm)	
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN	
Flow Rate:	1 mL/min	
Inj. Volume:	20 mL concentrated on AG5	
Detection:	Absorbance at 215 nm	
Temperature:	ambient	
Sample:	Spiked Groundwater	
Peaks:	1. $[Ag(CN)_2]^-$	100 µg/L
	2. $[Au(CN)_2]^-$	75
	3. $[Cu(CN)_3]^{2-}$	4
	4. $[Ni(CN)_4]^{2-}$	75
	5. $[Fe(CN)_6]^{4-}$	10
	6. $[Co(CN)_6]^{3-}$	100

These data are provided for guidance purposes only.

Figure taken from Reference 22.

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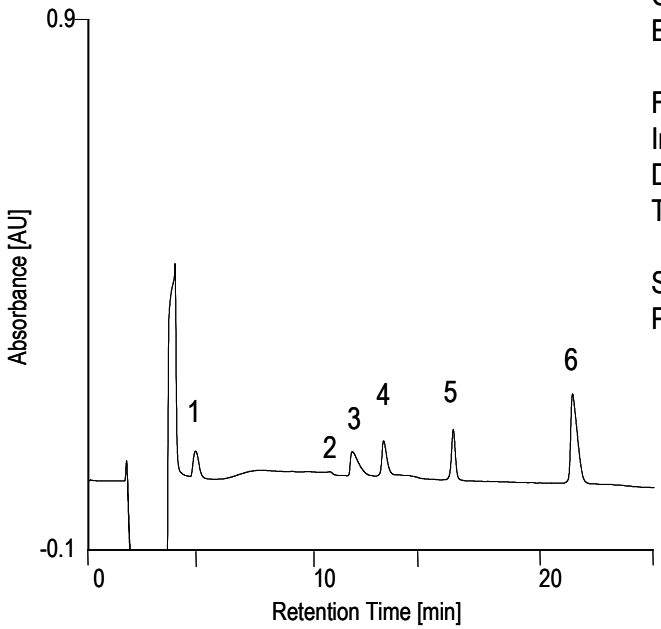
FIGURE 11

EXAMPLE SPIKED SOIL EXTRACT CHROMATOGRAM USING SAMPLE PRECONCENTRATION



Column:	IonPac® AS11 (2-mm)	
Eluent:	$NaClO_4$ gradient in 20 mM NaOH/15 mM NaCN	
Flow Rate:	0.25 mL/min	
Inj. Volume:	5 mL concentrated on AG11	
Detection:	Absorbance at 215 nm	
Temperature:	ambient	
Sample:	Spiked Soil Extract	
Peaks:	1. $[Ag(CN)_2]^-$	100 µg/L
	2. $[Cu(CN)_3]^{2-}$	4
	3. $[Au(CN)_2]^-$	75
	4. $[Ni(CN)_4]^{2-}$	75
	5. $[Fe(CN)_6]^{4-}$	10
	6. $[Co(CN)_6]^{3-}$	100

These data are provided for guidance purposes only.

Figure taken from Reference 22.

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Appendix A
Summary of Revisions to Method 9015 (from Revision 1, November 2004)

1. The entire document was formatted in Microsoft Word .docx format from the original .WPD and .PDF files. The revision number was changed to one and the date published to July 2014.
2. Minor editorial and grammatical changes were made throughout the document as needed.
3. Text regarding the IDP (Sec. 9.2) and LLOQ (9.7) consistent with SW-846 Chapter One was added.
4. Graphics in the Figures Section were modified from Corel Drawing Objects V.10 to .jpg graphical images (where needed) to remove artifacts from the conversion process. The text titles of each figure was centered and formatted.
5. This Appendix was added to document changes made during the editorial process.
6. Updated and expanded the “QUALITY CONTROL” section for better adherence to current SW-846 method guidelines and for improved alignment with current universal practices for published analytical methods.

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