Direct Determination of Metal Cyanides by Ion Chromatography with UV Absorbance Detection

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Introduction

Metal cyanide complexes are negatively charged ionic complexes consisting of one or more cyanide ions (CN^-) bound to a single transition metal cation. These complexes have the general formula $[M(CN)_b]^{x-}$, where M represents a transition metal cation (such as Ag^+, Au^+, Cu^+, Ni^{2+}, Fe^{2+}, Co^{3+}, etc.), b is the number of bound cyanide ions, and x is the total anionic charge of the complex. Metal cyanide complexes are of environmental concern because they release cyanide upon dissociation. In environmental waters below pH 9.3, the cyanide ion converts to HCN, an extremely toxic substance. Metal cyanide complexes are also of interest in the mining and reclamation of precious metals, and in the metal finishing industry.

Many metal cyanide complexes are relatively stable and require moderate to strongly acidic conditions to liberate cyanide. The stability of metal cyanide complexes with respect to dissociation is expressed by their formation constants, and shown in Table 1. As indicated in Table 1, metal cyanide complexes with formation constants greater than about 1035 are often termed "strong metal cyanide complexes". The distinction between weak and strong complexes is environmentally relevant because strong complexes such as iron (II) cyanide dissociate only under strongly acidic conditions (pH <2) and are considered relatively stable and nontoxic, whereas weak metal cyanide complexes dissociate under mildly acidic conditions (pH >3 but <6) to liberate cyanide.

Table 1. Stability of metal cyanide complexes.[8,9]

Metal Cyanide Complex	Stability Constant (log K at 25 °C)	Type of Complex
$[Co(CN)_6]^{3-}$	64	Strong
$[Fe(CN)_6]^{3-}$	43.6	Strong
$[Pd(CN)_4]^{2-}$	42.4	Strong
$[Pt(CN)_4]^{2-}$	40.0	Strong
$[Hg(CN)_4]^{2-}$	39.0	Strong
$[Au(CN)_2]^{-}$	37	Strong
$[Fe(CN)_6]^{4-}$	35.4	Strong
$[Ni(CN)_4]^{2-}$	30.2	Weak
$[Cu(CN)_4]^{3-}$	23.1	Weak
$[Cu(CN)_3]^{2-}$	N.A.*	Weak
$[Ag(CN)_2]^{-}$	20.5	Weak
$[Zn(CN)_4]^{2-}$	19.6	Weak
$[Cd(CN)_4]^{2-}$	17.9	Weak

* Data not available

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Previous methods that assess the potential toxicity due to cyanide directly measure only free cyanide, typically by a colorimetric reaction with a pyridine-barbituric acid reagent. These methods then rely on an operational definition to distinguish between weak and strong cyanide complexes, by subjecting the sample to increasingly harsh conditions to dissociate some fraction of the cyanide complexes and liberate free cyanide. Examples include methods that measure "cyanides amenable to chlorination",[1] "weak acid dissociable cyanides",[2] "available cyanide",[3] and "total cyanide".[4] The results are highly dependant on the matrix, the type of metal cyanide complexes present, and the procedure used. These methods also require time-consuming sample pretreatment or distillation to reduce interference from sulfides, chlorine, thiosulfate, and other compounds.

Ion chromatography (IC) is superior to the aforementioned methods because it resolves each individual metal cyanide complex into a discrete chromatographic peak. IC thus allows a precise differentiation of complexes of lesser toxicity from those of greater toxicity. This application update presents modifications to the IC method described in Dionex (now part of Thermo Scientific) Application Note 55.[5] The metal cyanide complexes of silver, gold, copper, nickel, iron, and cobalt ($[Ag(CN)_2]^-$, $[Au(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$) are separated on a 2 mm Thermo Scientific™ Dionex™ IonPac™ AS11 column and quantified by measuring their absorbance at 215 nm. Use of the 2 mm Dionex IonPac AG11/AS11 column set provides different selectivity, lower eluent use, and better solvent compatibility than the Dionex IonPac AG5/AS5 column set featured in Application Note 55. This application update also presents a thorough comparison of the performance expected from the different column sets, with data obtained during participation in a joint ASTM/EPA interlaboratory collaborative study to validate the use of IC for the determination of metal cyanide complexes in environmental waters. The method was evaluated for reproducibility, linearity, accuracy, precision, and spike recovery from various matrices.[6]

Equipment

Thermo Scientific Dionex ICS-2500* IC system consisting of:

- Thermo Scientific Dionex GP50 Gradient Pump
- Thermo Scientific Dionex AD25 Absorbance Detector
- Thermo Scientific™ Dionex™ AutoSelect™ AS50 Autosampler with Thermal Compartment
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System Workstation

Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-5000+ system

Consumables
- Syringe filters
- Storage bottles, amber HDPE

Conditions

Columns:	Dionex IonPac AS11 Analytical 2 × 250 mm Dionex IonPac AG11 Guard 2 × 50 mm Dionex IonPac ATC-3 (2 each)		
Temperature:	30 °C		
Injection:	25 µL		
Detection:	Absorbance at 215 nm		
Expected System Backpressure:	900 psi		
Noise:	1–5 mAU		
Run Time:	35 min		
Flow Rate:	0.25 mL/min		
Eluent A:	20 mM NaOH/150 mM NaCN		
Eluent B:	20 mM NaOH/300 mM NaClO$_4$		
Eluent C:	20 mM NaOH		
Pump Program:	Time (min)	%A	%B	%C
	Init.	10	10	80
	0.0	10	10	80
	18.0	10	45	45
	22.0	10	45	45
	25.0	10	10	80
	35.0	10	10	80

Reagents and Standards
- Sodium hydroxide solution 50% w/w
- Sodium cyanide, 99.99 %
- Sodium perchlorate monohydrate, HPLC-grade
- Copper cyanide
- Potassium ferrocyanide(II) trihydrate
- Potassium dicyanoargentate(I)
- Potassium dicyanoaurate(I)
- Potassium hexacyanocobaltate(III)
- Potassium tetracyanonickelate(II) monohydrate

Preparation of Solutions and Reagents

Prepare all solutions from analytical reagent-grade chemicals and Type I reagent-grade deionized water with a specific resistance of 18.0 MΩ-cm or greater, filtered through a 0.2 µm filter immediately before use.

Eluent Preparation
Eluent 1 (20 mM Sodium Hydroxide/150 mM Sodium Cyanide)
Use high-quality water of high resistivity (18.0 MΩ-cm or better) that contains as little dissolved carbon dioxide as possible. Biological contamination should be absent. Sodium hydroxide eluent should be prepared with 50% (w/w) sodium hydroxide solution. Sodium hydroxide pellets are covered with a thin layer of sodium carbonate and should not be used under any circumstances. Keep all eluents blanketed under helium at 34–55 kPa (5–8 psi) after preparation. If maintained under helium, this and the following eluents can be used for approximately one week.

To prepare 2 L of 20 mM NaOH/150 mM NaCN, place 14.70 g sodium cyanide into a 2 L volumetric flask containing 1.9 L of deionized water and degas for 20 min by sonicating under vacuum. Use a plastic pipette to deliver 2.08 mL (or 3.2 g) of 50% (w/w) sodium hydroxide. Bring to volume with degassed deionized water. Cap and invert the volumetric flask eight times to mix.

Note: Do not excessively mix, because this action will increase the carbonate ion in the solution by trapping carbon dioxide from the air.

Eluent 2 (20 mM Sodium Hydroxide/300 mM Sodium Perchlorate)

Place 84.20 g HPLC-grade sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$) into a 2 L volumetric flask containing 1.9 L of deionized water and degas for 20 min by sonicating under vacuum. Use a plastic pipette to deliver 2.08 mL (or 3.2 g) of 50% (w/w) sodium hydroxide. Bring to volume with degassed deionized water. Cap and invert the volumetric flask eight times to mix. Continue degassing for 10 min and then blanket with helium as described above.

Eluent 3 (20 mM Sodium Hydroxide)

Add 2.08 mL (or 3.2 g) of 50% (w/w) sodium hydroxide to a 2 L volumetric flask containing 1.9 L of degassed deionized water. Bring to volume with degassed deionized water. Cap and invert the volumetric flask eight times to mix. Continue degassing for 10 min and then blanket with helium as described above.

Diluent (10 mM Sodium Hydroxide)

Add 1.04 mL (1.6 g) of 50% (w/w) sodium hydroxide to a 2 L volumetric flask containing 1.9 L of degassed deionized water. Bring to volume with degassed deionized water. Cap and invert the volumetric flask eight times to mix. Continue degassing for 10 min.

Standard Preparation

Store the metal cyanide reagent salts in a dessicator protected from the light. To prepare stock standards (1000 mg/L) for each metal cyanide species, weigh the amount of the appropriate compound given in Table 2 into a 100 mL volumetric flask. Add enough 10 mM sodium hydroxide solution to dissolve the cyanide complex, bring to volume with 10 mM sodium hydroxide solution, mix, and transfer to an amber HDPE bottle. Store at 4–6 °C. The individual stock standards are stable under these conditions for the periods shown in Table 2.

Table 2. Preparation of metal cyanide stock standards.

Anion	Compound	Mass (g)	Stability** (days)
$[Ag(CN)_2]^-$	$KAg(CN)_2$	0.1244	1
$[Au(CN)_2]^-$	$KAu(CN)_2$	0.1157	30
$[Cu(CN)_3]^{2-}$	$Cu(CN)$ and $NaCN$	0.0632*	1
$[Ni(CN)_4]^{2-}$	$K_2Ni(CN)_4 \bullet H_2O$	0.1591***	1
$[Fe(CN)_6]^{4-}$	$K_4Fe(CN)_6 \bullet 3\,H_2O$	0.1993	30
$[Co(CN)_6]^{3-}$	$K_3Co(CN)_6$	0.1546	30

* Dissolve the CuCN with 0.1384 g sodium cyanide in a 100 mL volumetric flask containing 50 mL 10 mM sodium hydroxide solution. Bring to volume with 10 mM sodium hydroxide solution. Stir or sonicate for 1 h or until dissolved.

** Stability in number of days when stored in amber HDPE at 4–6 °C. Prepare fresh stock standards as needed according to this table.

*** Dissolve (1.4806 + 0.1107 × n) g of potassium nickle cyanide mono- or polyhydrate, $K_2[Ni(CN)_4] \bullet n\,H_2O$, where n = number of water molecules of hydration.

Precaution: Some of the metal cyanide complexes are very toxic. Avoid contact with water or acid. Clean up and appropriately dispose of any spills.

Prepare calibration standards spanning the linear calibration range of each analyte by diluting the 1000 mg/L stock standards with 10 mM sodium hydroxide solution. To prepare mixed standards, measure appropriate volumes of the 1000 mg/L standards into 100 mL volumetric flasks, bring to volume with 10 mM sodium hydroxide solution, mix, and transfer to an amber HDPE bottle. These mixed calibration standards should be prepared fresh on the day of use.

Table 3 shows the concentration of calibration standards prepared in this way for the ASTM study.

Table 3. Concentrations of metal cyanide calibration standards.

Anion	Concentration (mg/L)				
	Level 1	Level 2	Level 3	Level 4	Level 5
$[Ag(CN)_2]^-$	100	25	6.250	1.562	0.391
$[Au(CN)_2]^-$	50	12.50	3.125	0.781	0.195
$[Cu(CN)_3]^{2-}$	2.0	0.50	0.125	0.031	0.008
$[Ni(CN)_4]^{2-}$	200	50	12.50	3.125	0.781
$[Fe(CN)_6]^{4-}$	20	5.0	1.250	0.312	0.078
$[Co(CN)_6]^{3-}$	100	25	6.250	1.562	0.391

Sample Preparation

This section briefly summarizes the sample preparation procedure outlined in the ASTM/EPA draft method followed in the study. The ASTM study organizers provided six matrices and concentrated spiking solutions with instructions to spike each matrix at six levels. The six levels consisted of three pairs of closely spaced concentrations (Youden Pairs). The six matrices were deionized water, drinking water, groundwater, surface water, wastewater, and ocean water.

Upon collection, the samples were treated, if necessary, with powdered lead carbonate to remove sulfide interferences, and with sodium thiosulfate to remove interfering oxidants, in accordance with *Standard Methods*.[7] The samples were then adjusted with sodium hydroxide to pH = 12.5 and stored in amber bottles at 4–6 °C. Samples preserved in this way must be analyzed within 14 days. On the day of analysis, the samples were brought to room temperature, spiked with the spiking solutions, and then filtered through 0.22 µm nylon filters into the autosampler vials.

System Preparation and Setup

Verify that the pump flow rate is within specifications and recalibrate if necessary. A Dionex GP50 pump should deliver water at 1.0 ± 0.005 mL/min against a constant backpressure of 2000 psi. Verify that the UV/Vis absorbance detector wavelength accuracy is within specifications and recalibrate if necessary. It is a good practice to periodically record the visible lamp output (i.e., the reference cell current in nA) and elapsed time to aid in troubleshooting. Consult the pump or detector manuals for procedural details.

Install an Dionex IonPac ATC-3 column between the eluent reservoir containing sodium cyanide and the pump inlet. The Dionex IonPac ATC-3 column removes metal cyanide impurities present in the sodium cyanide solution that would otherwise cause elevated background noise. Regenerate the Dionex IonPac ATC-3 column as needed by using a trap column/suppressor cleanup kit according to the installation and instruction manual (Document No. 031835).

Install and configure the autosampler and thermal compartment with a 25 µL sample loop. The most accurate and precise injections are made with a calibrated sample loop flushed with about four loop volumes of sample before injection. Install a 250 µL sample syringe and set the "Syringe Speed" to 4 or 5. Enter the correct sample "Loop Size" and "Sample Syringe Volume" in the Thermo Scientific Dionex AS50 Plumbing Configuration Screen. Refer to the Dionex AutoSelect *AS50 Autosampler Operator's Manual* (Document No. 031169) for details. Install a gradient mixer and an Dionex IonPac ATC-3 column between the pump and injection valve.

Install a 2 × 50 mm Dionex IonPac AG11 column and a 2 × 250 mm Dionex IonPac AS11 column. Rinse the column with the ending eluent composition (10:45:45) for 30 min. Equilibrate the column with the initial eluent composition (10:10:80) for 10 min before analyzing a system blank of deionized water. In an equilibrated system, the background shift during the gradient run should be less than 100 mAU. The peak-to-peak noise and drift should not exceed 5 mAU/min. There should be no significant peaks eluting within the retention time windows of the metal cyanide analyte anions.

Inject a mid-level standard. The column is equilibrated when two consecutive injections of the standard produce the same retention time for the metal cyanide complex anions. Confirm that the resulting chromatogram resembles the chromatogram of the standard shown in Figure 1B.

Columns:	(A) Dionex IonPac AG5/AS5, 4 × 250 mm	
	(B) Dionex IonPac AG11/AS11, 2 × 250 mm	
Eluent:	(1) 20 mM sodium hydroxide/150 mM sodium cyanide	
	(2) 20 mM sodium hydroxide/300 mM sodium perchlorate	
	(3) 20 mM sodium hydroxide	
	Gradient from 10/10/80 to 10/45/45 in 18 min	
Temperature:	30 °C	
Flow Rate:	(A) 1.0 mL/min	
	(B) 0.25 mL/min	
Inj. Volume:	(A) 100 µL	
	(B) 25 µL	
Detection:	Absorbance at 215 nm	

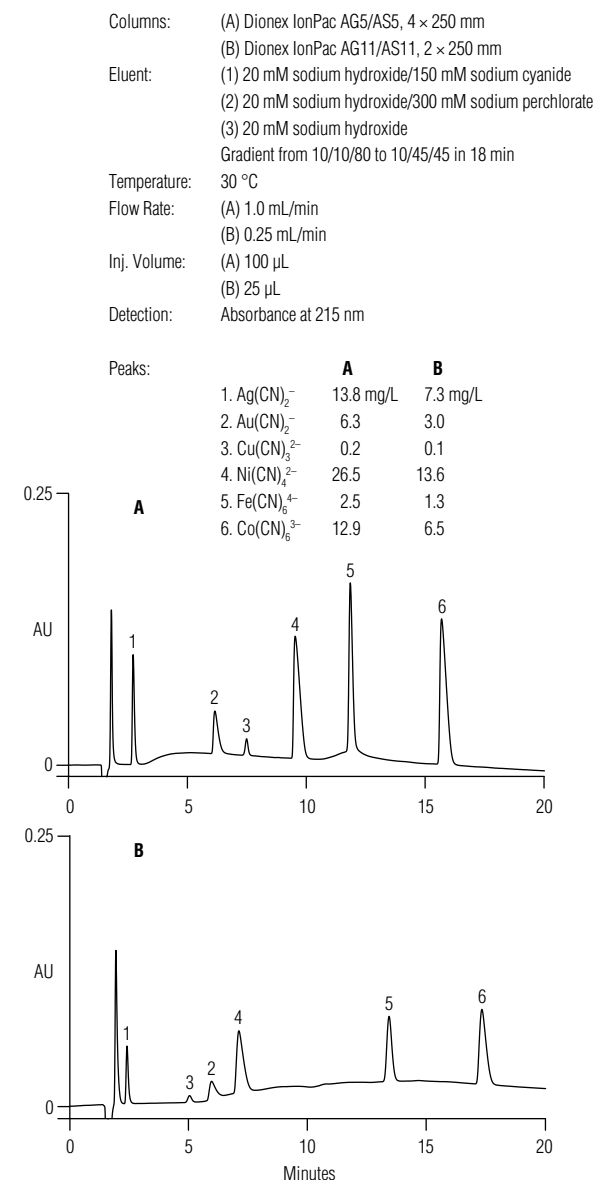| Peaks:	A	B
1. $Ag(CN)_2^-$	13.8 mg/L	7.3 mg/L
2. $Au(CN)_2^-$	6.3	3.0
3. $Cu(CN)_3^{2-}$	0.2	0.1
4. $Ni(CN)_4^{2-}$	26.5	13.6
5. $Fe(CN)_6^{4-}$	2.5	1.3
6. $Co(CN)_6^{3-}$	12.9	6.5

Figure 1. Anion-exchange separation with absorbance detection at 215 nm of metal cyanide complex standard on the (A) Dionex IonPac AS5 column and (B) Dionex IonPac AS11 column.

Table 4. Linear ranges and MDLs for metal cyanide complexes.

Analyte	Range (mg/L)	MDL Standard (mg/L)	r² AS5	r² AS11	MDL * AS5 (mg/L)	MDL * AS11 (mg/L)
$[Ag(CN)_2]^-$	1–100	5.0	0.99936	0.99921	0.18	1.48
$[Au(CN)_2]^-$	1–50	5.0	0.99994	0.99999	0.64	0.28
$[Cu(CN)_3]^{2-}$	0.1–2	0.1	0.99985	0.99993	0.08	0.06
$[Ni(CN)_4]^{2-}$	1–200	5.0	0.99992	0.99991	1.10	0.77
$[Fe(CN)_6]^{4-}$	0.1–20	0.5	0.99998	0.99999	0.12	0.09
$[Co(CN)_6]^{3-}$	1–100	5.0	0.99998	0.99996	0.54	0.50

*The MDLs were calculated as MDL = (t) × (S) Where t = Student's t value for a 99% confidence level and a standard deviation estimate with n - 1 degrees of freedom (t = 3.14 for seven replicates of the MDL Standard), and S = standard deviation of the replicate analysis.

Results and Discussion

Calibrate the system by injecting one blank and at least five standards for every two decades of the calibration range. Plot the peak area for each metal cyanide complex versus the concentration injected and use a linear regression to fit the data. Table 4 summarizes the calibration data for a typical calibration curve obtained by injecting calibration standards covering the ranges shown. The calibration curve is linear over two orders of magnitude for the silver, nickel, iron, and cobalt cyanide complexes. Copper cyanide and gold cyanide were calibrated over a smaller interval. On the Dionex IonPac AS11 column, the copper cyanide, gold cyanide, and nickel cyanide complexes begin to coelute at higher concentrations, requiring the analyst to judge where to split the peaks. The problem is less severe for nickel cyanide, the later-eluting peak. Any samples containing high levels of copper or gold cyanide should be diluted to a level where coelution does not occur. Note that because of differences in molar absorptivity at 215 nm among the metal cyanide complexes, the linear calibration range is significantly different from one complex to another.

Figure 1 compares the chromatograms of a calibration standard obtained by using either the Dionex IonPac AS5 or Dionex IonPac AS11 columns. Both chromatograms were obtained using the same eluent gradient program. Under these conditions, the Dionex IonPac AS5 column (1A) provides better separation of the gold, copper, and nickel cyanide complexes, whereas the Dionex IonPac AS11 column (1B) provides better separation between the nickel, iron, and cobalt cyanide complexes. These differences in selectivity can be exploited to improve certain analyses. For example, the Dionex IonPac AS11 column may better determine low levels of iron cyanide in the presence of high levels of nickel cyanide, because there is less likelihood of a large nickel cyanide peak obscuring a smaller iron cyanide peak. Note that the elution order of copper and gold is reversed on the two columns. Therefore, the Dionex IonPac AS5 column may better determine trace levels of gold cyanide in the presence of higher levels of copper cyanide. If necessary, experienced chromatographers can modify the eluent gradient program to optimize the separation for a particular analysis. One noteworthy feature of the 2 mm Dionex IonPac AS11 column is that it consumes 1/4 the eluent required by the 4 mm Dionex IonPac AS5 column—an important advantage that can lower reagent and waste disposal costs.

The limits of detection of this method were determined by making seven injections of deionized water, fortified with the analytes at levels yielding peaks approximately five times higher than the background noise. Column 3 of Table 4 shows the actual concentrations of the six metal cyanides analyzed. The formula given below Table 4 was used to calculate the minimum detection limit (MDL) for each analyte. Table 4 compares the calculated MDLs obtained on both the Dionex IonPac AS5 and Dionex IonPac AS11 columns.

Both columns provide minimum detection limits in the low-mg/L range for the tested metal cyanide complexes. Silver cyanide $[Ag(CN)_2]^-$ exhibits a significantly higher MDL on the Dionex IonPac AS11 column because the complex elutes considerably earlier, in an area that has interference from the tail of the matrix peak. This interference makes integration of the silver cyanide peak less reliable, and the precision of the peak area measurement is reduced. At the low concentrations analyzed in this application update, both columns also exhibit some interference with iron cyanide $[Fe(CN)_6]^{4-}$. On the Dionex IonPac AS5 column, the iron peak shows considerable tailing, whereas on the Dionex IonPac AS11 column, a small interfering peak is seen to coelute with iron. In both cases, the MDL for iron cyanide increases somewhat because of the interfering peak. It is possible that the interfering peak is from the unreduced iron (III) cyanide complex. If so, the Dionex IonPac AS11 column might succeed in resolving these two complexes with a minor change to the gradient program.

The next several chromatograms illustrate typical real-world results. Figure 2 compares the Dionex IonPac AS5 and Dionex IonPac AS11 columns when analyzing a groundwater sample. In this fairly low-ionic-strength matrix, the two columns provide comparable results, with the Dionex IonPac AS5 column (Figure 2A) better resolving the gold, copper, and nickel complexes, whereas the Dionex IonPac AS11 column (Figure 2B) exhibits less tailing of the iron cyanide peak and a better baseline in that region.

Figure 3 compares the Dionex IonPac AS5 and Dionex IonPac AS11 columns when analyzing a wastewater sample. In this high-ionic-strength matrix, the matrix ions elute as a very broad, tailing peak that poses a significant problem for recovery of silver cyanide. The Dionex IonPac AS5 column (Figure 3A) shows significantly better recovery for the silver cyanide complex because it is resolved slightly better from the matrix ions than on the Dionex IonPac AS11 column (Figure 3B). The peaks for the copper, gold, and nickel cyanide complexes are also more adversely affected on the Dionex IonPac AS11 column, though to a lesser extent than the silver cyanide complex.

Columns: (A) Dionex IonPac AG5/AS5, 4 × 250 mm
(B) Dionex IonPac AG11/AS11, 2 × 250 mm
Eluent: (1) 20 mM sodium hydroxide/150 mM sodium cyanide
(2) 20 mM sodium hydroxide/300 mM sodium perchlorate
(3) 20 mM sodium hydroxide
Gradient from 10/10/80 to 10/45/45 in 18 min
Temperature: 30 °C
Flow Rate: (A) 1.0 mL/min
(B) 0.25 mL/min
Inj. Volume: (A) 100 µL
(B) 25 µL
Detection: Absorbance at 215 nm

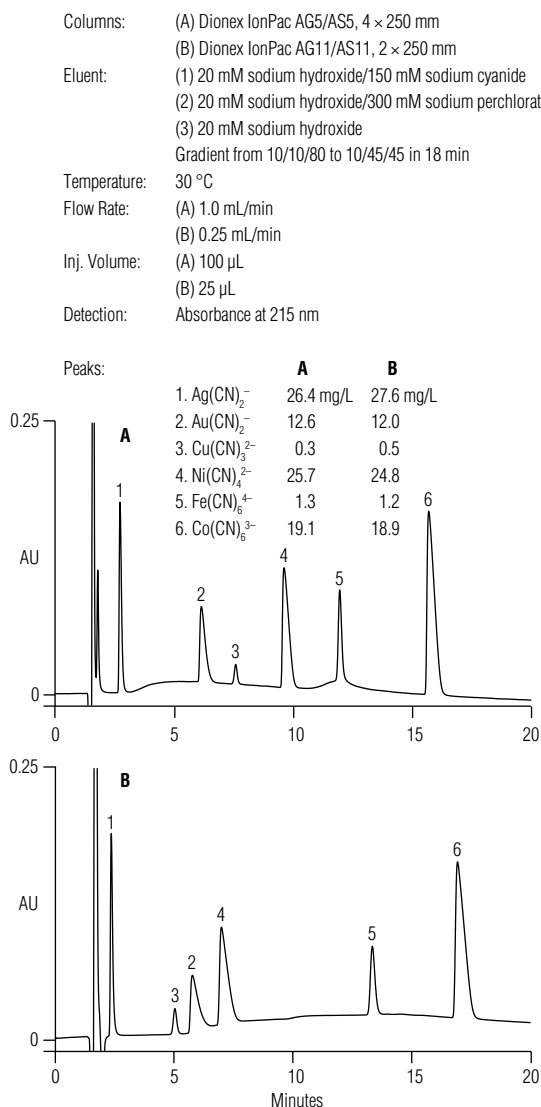| Peaks:		A	B
1. $Ag(CN)_2^-$		26.4 mg/L	27.6 mg/L
2. $Au(CN)_2^-$		12.6	12.0
3. $Cu(CN)_3^{2-}$		0.3	0.5
4. $Ni(CN)_4^{2-}$		25.7	24.8
5. $Fe(CN)_6^{4-}$		1.3	1.2
6. $Co(CN)_6^{3-}$		19.1	18.9

Figure 2. Determination of metal cyanide complexes in groundwater. Injection onto the (A) Dionex IonPac AS5 column and (B) Dionex IonPac AS11 column.

Columns: (A) Dionex IonPac AG5/AS5, 4 × 250 mm
(B) Dionex IonPac AG11/AS11, 2 × 250 mm
Eluent: (1) 20 mM sodium hydroxide/150 mM sodium cyanide
(2) 20 mM sodium hydroxide/300 mM sodium perchlorate
(3) 20 mM sodium hydroxide
Gradient from 10/10/80 to 10/45/45 in 18 min
Temperature: 30 °C
Flow Rate: (A) 1.0 mL/min
(B) 0.25 mL/min
Inj. Volume: (A) 100 µL
(B) 25 µL
Detection: Absorbance at 215 nm

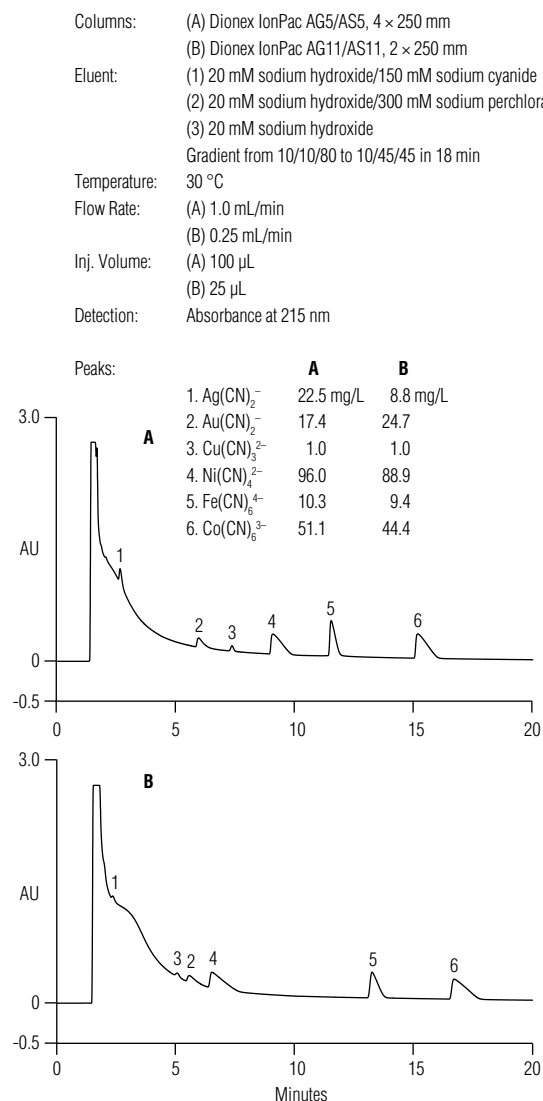| Peaks:		A	B
1. $Ag(CN)_2^-$		22.5 mg/L	8.8 mg/L
2. $Au(CN)_2^-$		17.4	24.7
3. $Cu(CN)_3^{2-}$		1.0	1.0
4. $Ni(CN)_4^{2-}$		96.0	88.9
5. $Fe(CN)_6^{4-}$		10.3	9.4
6. $Co(CN)_6^{3-}$		51.1	44.4

Figure 3. Determination of metal cyanide complexes in wastewater from a former manufactured gas plant. Injection onto the (A) Dionex IonPac AS5 column and (B) Dionex IonPac AS11 column.

Interferences

Exposure to light will cause photodecomposition of some metal cyanide complexes and reduce their concentration. Protect samples and standards from UV light by storing them in amber HDPE containers.

This method assumes that the alkaline conditions used will reduce iron (III) cyanide (ferricyanide) to iron (II) cyanide (ferrocyanide) resulting in a single peak for $[Fe(CN)_6]^{4-}$. Calibration is based on the iron (II) cyanide complex. Report results as mg/L of $[Fe(CN)_6]^{3-/4-}$ to represent the sum of ferrocyanide and ferricyanide. If unreduced $[Fe(CN)_6]^{3-}$ is present, it will elute as a tail on the iron ferrocyanide peak.

The sodium cyanide used to prepare eluent 1 may contain metal cyanide complex impurities. To reduce the level of these impurities, use 99.99% sodium cyanide to prepare the eluent, and install a Dionex IonPac ATC-3 anion trap column as described in this application update.

Precautions

Prepare all cyanide-containing solutions within a ventilation hood. Wear gloves, and avoid inhalation and skin or eye contact. Do not let acid contact any of the cyanide-containing samples, standards, or eluents. This contact would liberate hydrogen cyanide gas, an extremely toxic substance. Properly dispose of the old standards and eluent waste in accordance with applicable laws.

Strongly retained compounds from injected samples can accumulate on the column and degrade its performance. Signs of a fouled column include loss of capacity, loss of resolution, shortened retention times, higher noise and background, spurious peaks, and peak tailing. The Dionex IonPac AS11 column can be flushed with up to 100% acetonitrile to help remove contaminants from the column. The Dionex IonPac AS5 column cannot tolerate more than 5% organic solvent in the eluent. For more information on column troubleshooting and cleanup, see the *Installation Instructions and Troubleshooting Guide for the Dionex IonPac AS11 Analytical Column* (Document No. 034791).

Some groundwater samples contain particulates that will plug the column and increase the backpressure. Use a guard column to protect the analytical column; change the guard column if such a sample causes a sudden increase in total backpressure to greater than 3000 psi.

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