

# Determination of Metal Cyanide Complexes by Ion Chromatography with On-Line Sample Preconcentration and UV Absorbance Detection

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## Introduction

Metal cyanides are negatively charged ionic complexes represented by the general formula  $[M(CN)_b]^{x-}$ , where several cyanide ions are bound to a single transition metal cation such as  $Ag^+$ ,  $Au^+$ , or  $Fe_2^+$ . Metal cyanides can dissociate to release highly toxic HCN into the environment. The toxicity of metal cyanides varies widely from one species to another. Weak metal cyanides that readily dissociate, such as  $[Ag(CN)_2]^-$ , pose a significant threat to health, whereas strong metal cyanide complexes that dissociate only under strongly acidic conditions, such as  $[Fe(CN)_6]^{4-}$ , pose a lesser risk.

Several methods measure free cyanide, but rely on some operational definition to distinguish between weak and strong cyanide complexes. Examples include methods that measure “cyanides amenable to chlorination”,<sup>1</sup> “weak acid dissociable cyanides”,<sup>2</sup> and “total cyanide”<sup>3</sup> by subjecting the sample to increasingly harsh conditions to dissociate some fraction of the cyanide complexes and liberate free cyanide. The definitions are imprecise and highly dependent on the matrix and procedure used. These methods also require time consuming sample pretreatment, such as distillation to remove interferences, and even the distillate must be treated to remove interference from sulfides, chlorine, and thiosulfate.

Ion chromatography (IC) resolves each individual metal cyanide complex during an automated, 30 min separation. IC thus allows a precise differentiation of complexes of limited toxicity from those of greater toxicity.



Approval of a standard method based on IC will be of immediate benefit to those engaged in compliance monitoring or risk assessment of cyanide in the environment. To this end, we present an improved IC method that was subjected to a joint ASTM/EPA interlaboratory collaborative study to validate the use of IC for the determination of metal cyanide complexes in environmental waters. The metal cyanide complexes of silver, gold, copper, nickel, iron, and cobalt ( $[Ag(CN)_2]^-$ ,  $[Au(CN)_2]^-$ ,  $[Cu(CN)_3]^{2-}$ ,  $[Ni(CN)_4]^{2-}$ ,  $Fe(CN)_6]^{4-}$ , and  $[Co(CN)_6]^{3-}$ ) are separated on an anion-exchange column and quantified by measuring their absorbance at 215 nm. Sensitivity for most of the metal cyanide complexes is improved by over two orders of magnitude, compared to a direct injection,<sup>4</sup> by preconcentrating metal cyanide complexes from a large sample volume onto a trap column before separation. The method was evaluated for reproducibility, linearity, accuracy, precision, and spike recovery from various environmental water matrices.<sup>5</sup>

## Equipment

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

- Thermo Scientific Dionex GS50 Gradient Pump
- Thermo Scientific Dionex AD25 Absorbance Detector
- Thermo Scientific Dionex AutoSelect AS50 Autosampler, PEEK, with Chromatography Compartment and Chemistry Switching Option
- Thermo Scientific Dionex AS50 Dual-Valve Needle Assembly
- Sample PREP Syringe, 10 mL
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) Workstation
- Thermo Scientific Dionex DQP-1 Sample/Reagent Pump

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

## Consumables

- Syringe filters
- Storage bottles, amber HDPE
- Thermo Scientific Dionex MFC-1 Metal-Free Trap Column, 2 each
- Vial Kit 10 mL polystyrene

## Reagents and Standards

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

## Conditions

Columns:	Thermo Scientific™ Dionex™ IonPac™ AS11 Analytical, 2 × 250 mm Dionex IonPac AG11 Guard, 2 × 50 mm, 2 each Dionex IonPac ATC-3	Col_B	Flow =	0.25
Temperature:	30 °C		%B =	10.0
Injection:	5 mL		%C =	80.0
Detection:	Absorbance at 215 nm		%D =	0.0
Expected System			Curve =	5
Backpressure:	850 psi		Load	
Noise:	1–5 mAU		Inject	
Run Time:	32 min	10.000 Col_A	Flow =	0.25
Flow Rate:	0.25 mL/min		%B =	10.0
Eluent A:	20 mM sodium hydroxide/150 mM sodium cyanide		%C =	80.0
Eluent B:	20 mM sodium hydroxide/300 mM sodium perchlorate		%D =	0.0
Eluent C:	20 mM sodium hydroxide		Curve =	5
Program:		10.200 Autozero	UV_VIS_1.AcqOn	
0.000	Pressure.LowerLimit = 80		Flow =	0.25
	Pressure.UpperLimit = 3000		%B =	10.0
	%A.Equate = "Eluent A 150 mM NaCN"		%C =	80.0
	%B.Equate = "Eluent B 300 mM NaClO <sub>4</sub> "		%D =	0.0
	%C.Equate = "Eluent C 20 mM NaOH"		Curve =	5
	%D.Equate = "%D"	28.200	Flow =	0.25
	Sampler.Prime Volume = 2000, PrimeReservoir = Flush_Reservoir, PrimeSyringe = Sample		%B =	45.0
	SyringeSpeed = 2		%C =	45.0
	NeedleHeight = 2		%D =	0.0
	TrayTemperature = Off		Curve =	5
	Data_Collection_Rate = 5.00	32.200	UV_VIS_1.AcqOff	
	Rise_Time = 2.0		Flow =	0.25
	Wavelength = 215		%B =	45.0
	UV_Lamp = On		%C =	45.0
	Visible_Lamp = Off		%D =	0.0
	WaitForTemperature = False		Curve =	5
			End	

## Preparation of Solutions and Reagents

*Caution: Sodium cyanide and some of the metal cyanide complexes are very toxic. Avoid contact with water or acid. Clean up and properly dispose of any spills.*

Prepare all solutions from analytical reagent-grade chemicals. Use ASTM Type I reagent-grade water with a specific resistance of 18.0 MΩ-cm or greater. Filter the water through a 0.2 μm filter immediately before use and degas by sonicating under vacuum or sparging with helium for 10–15 min.

Always prepare sodium hydroxide eluents with 50% (w/w) sodium hydroxide solution. (Do not use sodium hydroxide pellets; they are covered with a thin layer of sodium carbonate that will cause irreproducible results). Keep all eluents blanketed under helium at 34–55 kPa (5–8 psi) after preparation. Properly dispose of old eluent and prepare fresh after one week.

### Eluent Preparation

#### Eluent A

##### (20 mM Sodium Hydroxide/150 mM Sodium Cyanide)

Place 14.70 g sodium cyanide into a 2 L volumetric flask containing 1.9 L of degassed reagent water. Use a plastic pipette to deliver 2.08 mL (or 3.2 g) of 50% (w/w) sodium hydroxide. Bring to volume with degassed reagent water. Cap and invert the volumetric flask eight times to mix. (Note: Do not excessively mix, as this will increase the carbonate ion in the solution by trapping carbon dioxide from the air). Blanket with helium as described above.

#### Eluent B

##### (20 mM Sodium Hydroxide/300 mM Sodium Perchlorate)

Place 84.20 g HPLC-grade sodium perchlorate monohydrate (NaClO<sub>4</sub> • H<sub>2</sub>O) into a 2 L container containing 1.9 L of reagent water and degas for 20 min by sonicating under vacuum. Transfer to a 2 L volumetric flask. Use a plastic pipette to deliver 2.08 mL (or 3.2 g) of 50% (w/w) sodium hydroxide. Bring to volume with degassed reagent water. Cap and invert the volumetric flask eight times to mix. Blanket with helium as described above.

#### Eluent C

##### (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 reagent water. Bring to volume with degassed reagent water. Cap and invert the volumetric flask eight times to mix. Blanket with helium as described above.

### Standard Preparation

Store the metal cyanide reagent salts in a desiccator protected from the light. Prepare 1000 mg/L stock standards of each metal cyanide complex by consulting Table 1. Weigh the reagent salt into a 100 mL volumetric flask. Add enough 20 mM sodium hydroxide solution to dissolve, bring to volume with the 20 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 1.

Table 1. Preparation of metal cyanide stock standards.

Anion	Compound	Mass (g)	Stability** (days)
[Ag(CN) <sub>2</sub> ] <sup>-</sup>	KAg(CN) <sub>2</sub>	0.1244	1
[Au(CN) <sub>2</sub> ] <sup>-</sup>	KAu(CN) <sub>2</sub>	0.1157	30
[Cu(CN) <sub>3</sub> ] <sup>2-</sup>	Cu(CN) and NaCN	0.0632*	1
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	K <sub>2</sub> Ni(CN) <sub>4</sub> •H <sub>2</sub> O	0.1591***	1
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	K <sub>4</sub> Fe(CN) <sub>6</sub> •3H <sub>2</sub> O	0.1993	30
[Co(CN) <sub>6</sub> ] <sup>3-</sup>	K <sub>3</sub> Co(CN) <sub>6</sub>	0.1546	30

\* Dissolve the CuCN with 0.138 g sodium cyanide in a 100 mL volumetric flask containing 50 mL 20 mM sodium hydroxide solution. Bring to volume with 20 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 nickel cyanide mono- or polyhydrate, [K<sub>2</sub>Ni(CN)<sub>4</sub>]•nH<sub>2</sub>O, where n = number of water molecules of hydration.

Prepare calibration standards spanning the linear calibration range of each analyte by diluting the 1000 mg/L stock standards with 20 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 the 20 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 2 shows the concentration of calibration standards prepared in this way for the ASTM study.

Table 2. Metal cyanide calibration standards.

Anion	Concentration (μg/L)				
	Level 1	Level 2	Level 3	Level 4	Level 5
[Ag(CN) <sub>2</sub> ] <sup>-</sup>	125	62.5	31.2	15.6	7.81
[Au(CN) <sub>2</sub> ] <sup>-</sup>	100	50.0	25.0	12.5	6.25
[Cu(CN) <sub>3</sub> ] <sup>2-</sup>	5.00	2.50	1.25	0.63	0.31
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	100	50.0	25.0	12.5	6.25
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	20.0	10.0	5.00	2.50	1.25
[Co(CN) <sub>6</sub> ] <sup>3-</sup>	200	100	50.0	25.0	12.5

## 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 included reagent water, drinking water, groundwater, groundwater from a manufactured gas plant (MGP) site, surface water, and wastewater.

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*.<sup>6</sup> 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 manner 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 IC syringe filters into the autosampler vials.

## System Preparation and Setup

Verify that the Dionex GS50 pump flow rate is within specifications and recalibrate if necessary. A Dionex GS50 pump should deliver water at  $1.0 \pm 0.005$  mL/min against a constant backpressure of 2000 psi. The Dionex DQP-1 pump used for sample preconcentration performs best with moderate headpressure on its inlet side and backpressure on its outlet side. Pressurize the reagent water reservoir to 34–55 kPa (5–8 psi) with compressed air, nitrogen or helium. Plumb a 5–10 foot long piece of red 0.005 in. i.d. PEEK tubing between the Dionex DQP-1 pump and Dionex MFC-1 trap column, before the column valve. Adjust the length of the tubing to provide 100–200 psi of backpressure. Then adjust the Dionex DQP-1 pump to deliver a flow rate of 1 mL/min against the backpressure that results during the preconcentration step. The Dionex DQP-1 pump should be left on continuously during a day's run; refill the reagent water reservoir as needed. Verify that the Dionex UV-Vis absorbance detector wavelength accuracy is within specifications and recalibrate if necessary. Consult the pump or detector manuals for procedural details. Keep a record of the Dionex AD25 reference cell current and the UV lamp's elapsed time. This information may prove useful for troubleshooting.

Prepare the eluents and set up the system as depicted in Figure 1. Using this system, the Dionex AutoSelect AS50 autosampler uses 8 mL of sample to flush and fill the 5 mL sample loop. At Time = 0, the inject valve moves to the inject position, allowing the Dionex DQP-1 pump to preconcentrate the 5 mL of sample onto the Dionex IonPac AG11 concentrator column at 1 mL/min for 10 min. At Time = 10 min, the column valve switches to "Column A" to place the preconcentrator column in-line with the Dionex IonPac AG11/AS11 separatory columns. At Time = 10.2 min, the eluent gradient begins and the metal cyanide complexes are separated. See Figures 2–4 for details of the valve switching process.

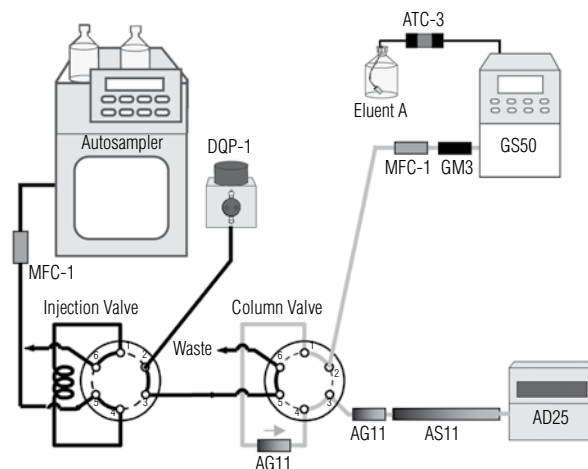


Figure 1. Diagram of the system used for determination of metal cyanide complexes by IC with on-line sample preconcentration.

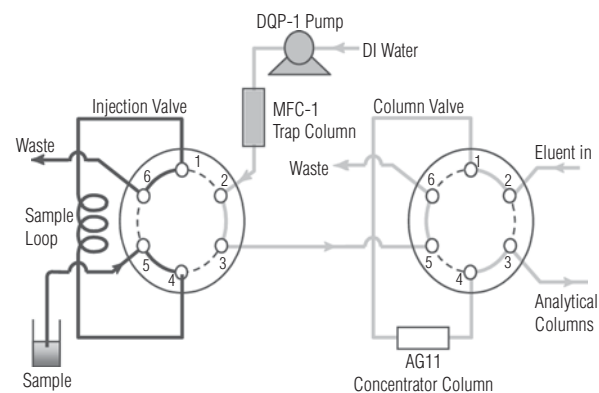


Figure 2. Schematic of an IC system during loading of the sample loop.

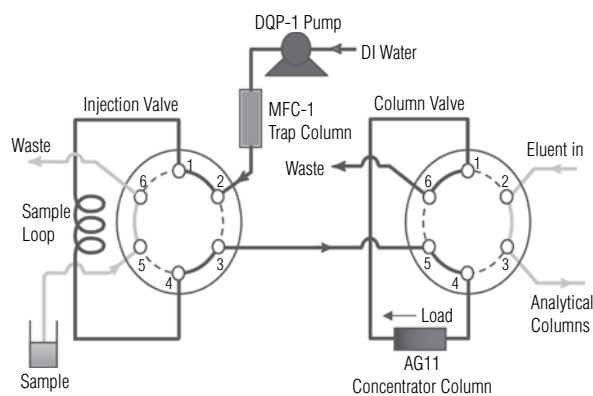


Figure 3. Schematic of an IC system during pre-concentration of the sample on the Dionex IonPac AG11 column.

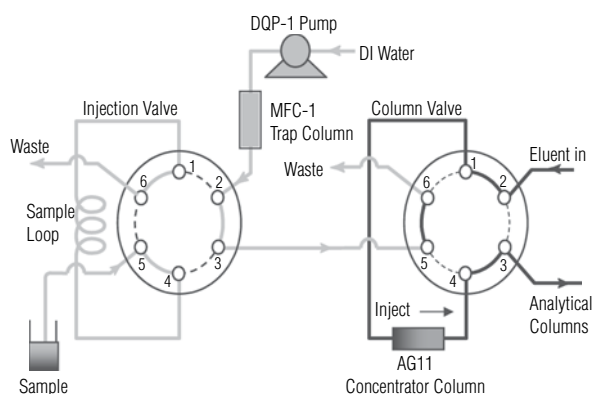


Figure 4. Schematic of an IC system during separation of the metal cyanide complexes.

Install an Dionex IonPac ATC-3 column between eluent reservoir A 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.

Install and configure the autosampler with the Dionex AS50 dual-valve needle assembly. Install a 10 mL sample syringe and enter a “Sample Syringe Volume” of 1 mL in the Dionex AS50 Plumbing Configuration Screen. Install a 5 mL sample loop between ports 1 and 4 of the injection valve and enter a “Sample Loop Size” of 200  $\mu\text{L}$  in the Dionex AS50 Plumbing Configuration Screen. When setting up the sequence, enter an “Injection Volume” of 200  $\mu\text{L}$ . The Dionex AutoSelect AS50 autosampler will then draw 8 mL of sample and use it to fill the 5 mL sample loop. Set the “Syringe Speed” to 3. (Important: setting the syringe speed too high may cause the inject port to leak during loading of the sample loop.) Install the 2 mm Dionex IonPac AG11 preconcentrator column between ports 1 and 4 of the column valve. Refer to the operator’s manual for the Dionex AutoSelect AS50 AutoSampler and the Dionex AS50 large-volume sampling needle assembly instructions for details.

Install a 2  $\times$  50 mm Dionex IonPac AG11 and 2  $\times$  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, such as the Level 2 standard in Table 2. 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 5B.

## 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 3 summarizes the calibration data for a typical calibration curve obtained by injecting calibration standards covering the ranges shown. The calibration curve is linear over about one and one-half orders of magnitude for each of the complexes. On the Dionex IonPac AS11 column, the copper cyanide, gold cyanide, and nickel cyanide complexes begin to coelute at higher concentrations. When running samples that contain a high concentration of either of these metal cyanide complexes, dilute the samples as needed to resolve these peaks. If necessary, modify the eluent gradient program to optimize the separation for a particular analysis.

Table 3. Linear ranges and MDLs for metal cyanide complexes.

Analyte	Range ( $\mu\text{g/L}$ )	MDL Standard ( $\mu\text{g/L}$ )	$r^2$	MDL* ( $\mu\text{g/L}$ )
$[\text{Ag}(\text{CN})_2]^-$	8–125	15	0.99611	1.08
$[\text{Au}(\text{CN})_2]^-$	6–100	10	0.99931	1.92
$[\text{Cu}(\text{CN})_3]^{2-}$	0.3–5	0.8	0.98538	0.41
$[\text{Ni}(\text{CN})_4]^{2-}$	6–100	50	0.99523	4.11
$[\text{Fe}(\text{CN})_6]^{4-}$	1–20	1.0	0.99995	0.17
$[\text{Co}(\text{CN})_6]^{3-}$	12–200	10	0.99999	2.20

\*  $\text{MDL} = (t) \times (S)$  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.



To determine method detection limits (MDLs) for this method, make seven injections of reagent water fortified with metal cyanide complexes at concentrations yielding peaks approximately five times higher than the background noise. In column 3 of Table 1, we list the concentrations of six metal cyanides analyzed for this application note, and the resulting MDLs. Note that the concentrations of the silver cyanide and nickel cyanide complexes were higher than recommended above—because the concentrations used were specified by the collaborative study organizers. (The formula given below Table 1 was used to calculate the MDL for each analyte.) MDLs are in the low- $\mu\text{g/L}$  range for the metal cyanide complexes in reagent water, varying mostly because of differences in molar absorptivity at 215 nm among the metal cyanide complexes. At the low concentrations analyzed in this application note, a small interfering peak was observed to coelute with copper cyanide  $[\text{Cu}(\text{CN})_3]^{2-}$ . This interferent increases the MDL for copper cyanide. Careful attention to regenerating the Dionex MFC-1 columns when necessary should keep this peak to a minimum.

Figures 5–8 are typical chromatograms obtained for each of the matrices analyzed in the ASTM/EPA collaborative study. Each figure displays the matrix blank along with the matrix spiked with metal cyanide complexes at concentrations approximating a mid-level standard. The actual concentrations vary somewhat because they were adjusted as needed to suit each matrix. Table 4 summarizes the spike concentrations and spike recovery data for each of the matrices. A few of the chromatograms are discussed below.

Figure 5A is the chromatogram of a reagent water blank and Figure 5B is reagent water fortified with metal cyanides. Table 4 summarizes the percent recovery of metal cyanides spiked into this matrix.

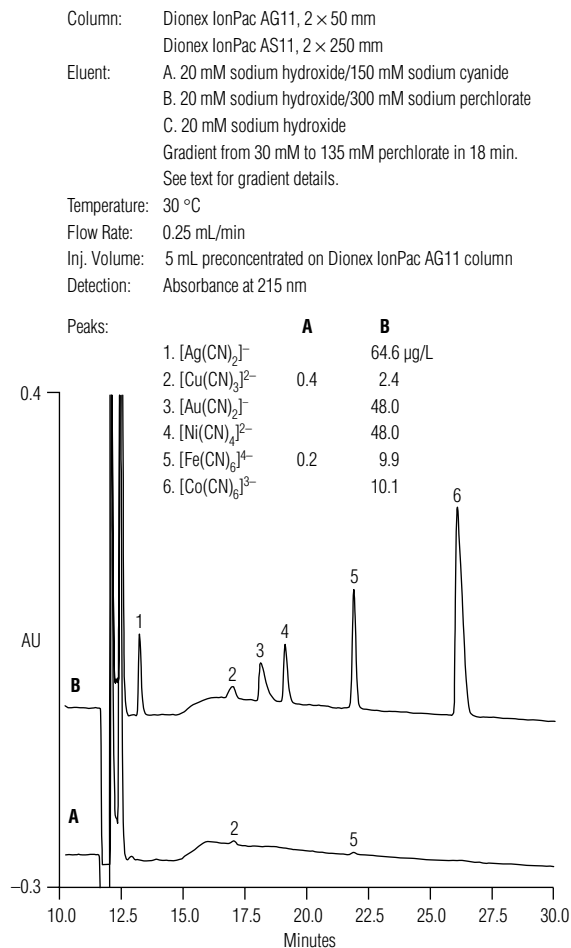


Figure 5. Anion-exchange separation with pre-concentration and absorbance detection at 215 nm of metal cyanide complexes in reagent water. Reagent water matrix blank (A) and matrix spiked with metal cyanide complexes as shown (B).

Table 4. Recovery of metal cyanide complexes from environmental waters.

Anion	% Recovery				
	Deionized Water	Drinking Water	Surface Water	Ground-water	Waste-water
$[\text{Ag}(\text{CN})_2]^-$	63.6	82.3	54.3	51.1	30.84
$[\text{Au}(\text{CN})_2]^-$	107	110	82.4	120	92.6
$[\text{Cu}(\text{CN})_3]^{2-}$	121	408	41.9	18.0	38.0
$[\text{Ni}(\text{CN})_4]^{2-}$	99.4	76.3	88.2	104	2.52
$[\text{Fe}(\text{CN})_6]^{4-}$	101	99.9	100	99.5	97.2
$[\text{Co}(\text{CN})_6]^{3-}$	99.0	105	105	100	99.9

Column: Dionex IonPac AG11, 2 × 50 mm  
 Dionex IonPac AS11, 2 × 250 mm  
 Eluent: A. 20 mM sodium hydroxide/150 mM sodium cyanide  
 B. 20 mM sodium hydroxide/300 mM sodium perchlorate  
 C. 20 mM sodium hydroxide  
 Gradient from 30 mM to 135 mM perchlorate in 18 min  
 See text for gradient details.

Temperature: 30 °C  
 Flow Rate: 0.25 mL/min  
 Inj. Volume: 5 mL pre-concentrated on Dionex IonPac AG11 column  
 Detection: Absorbance at 215 nm

Peaks:	A	B
1. $[\text{Ag}(\text{CN})_2]^-$	8.6	79.5 $\mu\text{g/L}$
2. $[\text{Cu}(\text{CN})_3]^{2-}$	1.1	16.1
3. $[\text{Au}(\text{CN})_2]^-$		83.7
4. $[\text{Ni}(\text{CN})_4]^{2-}$		60.8
5. $[\text{Fe}(\text{CN})_6]^{4-}$	0.1	10.1
6. $[\text{Co}(\text{CN})_6]^{3-}$	1.2	10.7

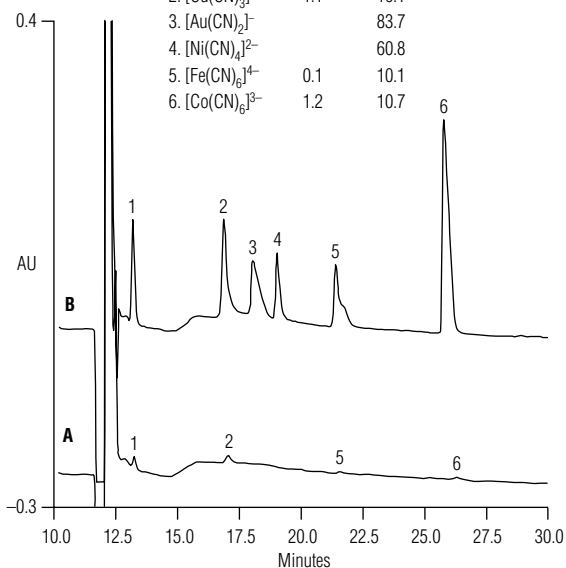


Figure 6. Anion-exchange separation with pre-concentration and absorbance detection at 215 nm of metal cyanide complexes in drinking water from a municipal well. Drinking water matrix blank (A) and matrix spiked with metal cyanide complexes (B) as shown.

Figure 6A is the chromatogram of drinking water from a municipal well. The matrix blank shows some traces of the silver, copper, iron, and cobalt cyanides. The spiked matrix yielded good recoveries for all the analytes, except copper cyanide, which was biased high. A matrix interferent is present just after the iron cyanide peak in Figure 6B.

Column: Dionex IonPac AG11, 2 × 50 mm  
 Dionex IonPac AS11, 2 × 250 mm  
 Eluent: A. 20 mM sodium hydroxide/150 mM sodium cyanide  
 B. 20 mM sodium hydroxide/300 mM sodium perchlorate  
 C. 20 mM sodium hydroxide  
 Gradient from 30 mM to 135 mM perchlorate in 18 min  
 See text for gradient details.

Temperature: 30 °C  
 Flow Rate: 0.25 mL/min  
 Inj. Volume: 5 mL pre-concentrated on Dionex IonPac AG11 column  
 Detection: Absorbance at 215 nm

Peaks:	A	B
1. $[\text{Ag}(\text{CN})_2]^-$	8.6	53.3 $\mu\text{g/L}$
2. $[\text{Cu}(\text{CN})_3]^{2-}$	0.1	0.7
3. $[\text{Au}(\text{CN})_2]^-$		80.8
4. $[\text{Ni}(\text{CN})_4]^{2-}$		89.6
5. $[\text{Fe}(\text{CN})_6]^{4-}$		12.8
6. $[\text{Co}(\text{CN})_6]^{3-}$	4.6	13.4

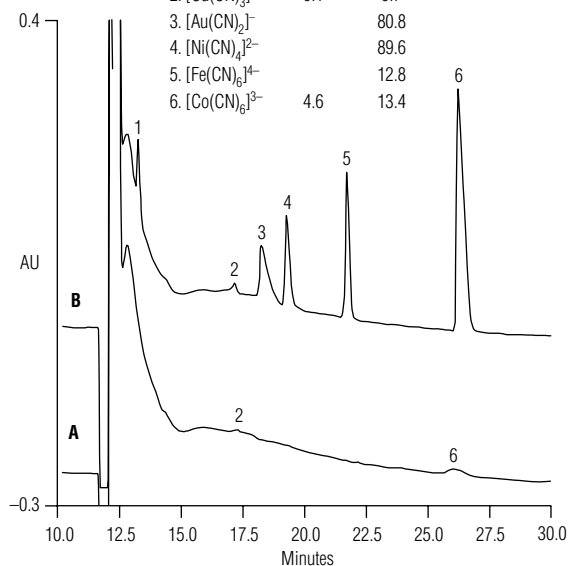


Figure 7. Anion-exchange separation with pre-concentration and absorbance detection at 215 nm of metal cyanide complexes in surface water from an industrial site. Surface water matrix blank (A) and matrix spiked with metal cyanide complexes (B) as shown.

Figure 7A is the chromatogram of a surface water sample from an industrial waste site. The matrix ions elute as a broad, tailing peak in this sample. This matrix may contain significant concentrations of bicarbonate or UV-absorbing organic substances. Traces of copper and cobalt cyanide complexes are observed in the matrix blank. In the spiked sample of Figure 7B, the matrix peak adversely affects the recovery of silver cyanide that elutes on the matrix peak's tailing baseline, and copper cyanide is biased low, as discussed below. The other metal cyanide complexes are unaffected and show good recoveries in Table 4.

Figure 8A is the chromatogram of a groundwater sample from a manufactured gas plant (MGP) site. This chromatogram exhibits tailing of the initial matrix ion peak similar to that observed in the surface water sample. Traces of the iron and cobalt cyanide complexes are seen in the matrix blank, along with a prominent unknown that elutes at 19–20 min. This peak has been observed in many samples taken from old MGP sites, and has been tentatively identified as a different iron cyanide complex.

### Interferences

Exposure to light causes photodecomposition of some metal cyanide complexes and reduces 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  $[\text{Fe}(\text{CN})_6]^{4-}$ . Calibration is based on the iron (II) cyanide complex. Report results as mg/L of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  so as to represent the sum of ferrocyanide and ferricyanide. If unreduced  $[\text{Fe}(\text{CN})_6]^{3-}$  is present, it elutes as a tail on the iron ferrocyanide peak.

The sodium cyanide used to prepare Eluent A may contain metal cyanide complex impurities. Reduce the level of these impurities by using 99.99% sodium cyanide to prepare the eluent, and by installing an Dionex IonPac ATC-3 anion trap column as described in this application note.

### Precautions

Prepare all cyanide-containing solutions within a ventilation hood. Wear gloves, avoid inhalation, and avoid skin or eye contact. Do not let acid contact any of the cyanide-containing samples, standards, or eluents. Such contact will liberate hydrogen cyanide gas, an extremely toxic substance. Dispose of the 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. 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 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.

Column: Dionex IonPac AG11, 2 × 50 mm  
Dionex IonPac AS11, 2 × 250 mm  
Eluent: A. 20 mM sodium hydroxide/150 mM sodium cyanide  
B. 20 mM sodium hydroxide/300 mM sodium perchlorate  
C. 20 mM sodium hydroxide  
Gradient from 30 mM to 135 mM perchlorate in 18 min  
See text for gradient details.  
Temperature: 30 °C  
Flow Rate: 0.25 mL/min  
Inj. Volume: 5 mL, pre-concentrated on Dionex IonPac AG11 column  
Detection: Absorbance at 215 nm

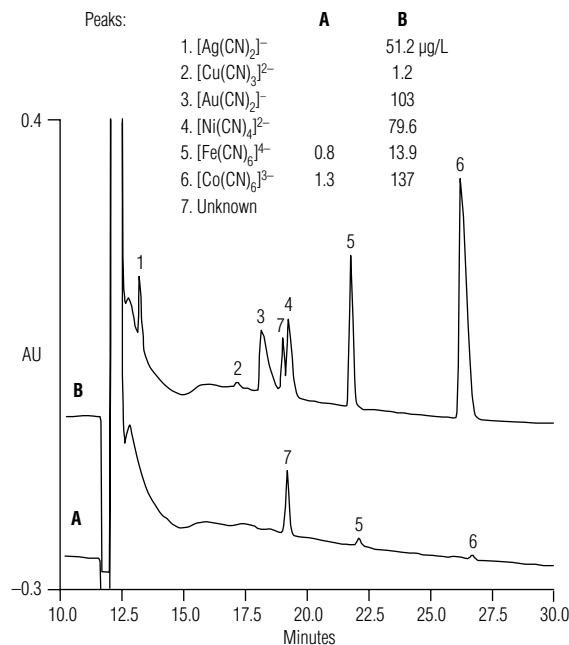


Figure 8. Anion-exchange separation with preconcentration and absorbance detection at 215 nm of metal cyanide complexes in groundwater from a manufactured gas plant (MGP) site. Groundwater matrix blank (A) and matrix spiked with metal cyanide complexes (B) as shown.

### Conclusion

This method of on-line preconcentration allows determination of metal cyanide complexes at µg/L concentrations in a variety of environmental water matrices. This method provides good recoveries for the gold, iron, and cobalt cyanide complexes in all matrices studied, and for the nickel cyanide complex in all matrices except wastewater. This method shows increased bias for the silver and copper cyanide complexes, especially in higher-ionic strength matrices. The low recoveries for the early-eluting silver cyanide complex result from interference by the matrix ions peak, and possibly some loss of the silver cyanide complex from the concentrator column during preconcentration. Low recovery of the copper cyanide complex may result from dissociation of the complex in high-ionic-strength matrices; an unknown coeluting species may impair determination of low concentrations of the copper cyanide complex.



## References

1. *Standard Methods for the Examination of Water and Wastewater*. 17th Edition, 1989. APHA-AWWAWPCF. 4500-CN B., pp 4–34.
2. Ibid, p 38.
3. Ibid, p 28.
4. Thermo Fisher Scientific. Thermo Scientific Application Update 147: Direct Determination of Metal Cyanides by Ion Chromatography with UV Absorbance Detection. Sunnyvale, CA, 2014.
5. *WK2791 Standard Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water using Anion Exchange Chromatography with UV Detection; ASTM International*; West Conshohocken, PA.
6. *Standard Methods for the Examination of Water and Wastewater*. 17th Edition, 1989. APHA-AWWAWPCF. 4500-CN B., pp 4–25.

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