

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

## INTRODUCTION

Metal cyanides are negatively charged ionic complexes represented by the general formula  $[M(CN)_6]^{x-}$ , 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>

Now sold under the  
Thermo Scientific brand

**Thermo**  
SCIENTIFIC

## EQUIPMENT

Dionex ICS-2500 IC system consisting of:

GS50 Gradient Pump

AD25 Absorbance Detector

AS50 AutoSelect, PEEK, with Chromatography  
Compartment and Chemistry Switching  
Option

AS50 Dual-Valve Needle Assembly  
(P/N 061267-01)

Sample PREP Syringe, 10-mL (P/N 055068)

Chromeleon® Chromatography Workstation

DQP-1 Sample/Reagent Pump (P/N 035250)

## Consumables

Syringe filters (Gelman IC Acrodisk® 0.2-µm, PN 4483)

Storage bottles, amber HDPE (VWR IRN301-0125 or  
16172-144)

Trap Columns, Metal-Free MFC-1, 2 each (P/N 037017)

Vial Kit 10-mL polystyrene (P/N 055058)

## CONDITIONS

Columns: IonPac® AS11 Analytical, 2 × 250 mm  
(P/N 44076)

IonPac AG11 Guard, 2 × 50 mm, 2 each  
(P/N 44078)

IonPac ATC-3 (P/N 059660)

Temperature: 30 °C

Injection: 5 mL

Detection: Absorbance at 215 nm

Expected System

Backpressure: 850 psi

Noise: 1–5 mAU

Run Time: 32 min

Flow Rate: 0.25 mL/min

Eluent A: 20 mM sodium hydroxide/150 mM  
sodium cyanide

Eluent B: 20 mM sodium hydroxide/300 mM  
sodium perchlorate

Eluent C: 20 mM sodium hydroxide

Program:

0.000 Pressure.LowerLimit = 80  
Pressure.UpperLimit = 3000  
%A.Equate = "Eluent A 150 mM  
NaCN"  
%B.Equate = "Eluent B 300 mM  
NaClO<sub>4</sub>"  
%C.Equate = "Eluent C 20 mM  
NaOH"  
%D.Equate = "%D"  
Sampler.Prime Volume=2000,  
PrimeReservoir=  
Flush\_Reservoir,  
PrimeSyringe=Sample  
SyringeSpeed = 2  
NeedleHeight = 2  
TrayTemperature = Off  
Data\_Collection\_Rate = 5.00  
Rise\_Time = 2.0  
Wavelength = 215  
UV\_Lamp = On  
Visible\_Lamp = Off  
WaitForTemperature = False  
Col\_B  
Flow = 0.25  
%B = 10.0  
%C = 80.0  
%D = 0.0  
Curve = 5  
Load  
Inject  
10.000 Col\_A  
Flow = 0.25  
%B = 10.0  
%C = 80.0  
%D = 0.0  
Curve = 5  
10.200 Autozero  
UV\_VIS\_1.AcqOn  
Flow = 0.25  
%B = 10.0  
%C = 80.0  
%D = 0.0  
Curve = 5

28.200 Flow = 0.25  
%B = 45.0  
%C = 45.0  
%D = 0.0  
Curve = 5

32.200 UV\_VIS\_1.AcqOff  
Flow = 0.25  
%B = 45.0  
%C = 45.0  
%D = 0.0  
Curve = 5  
End

### REAGENTS AND STANDARDS

Copper cyanide (AlfaAesar 12135)  
Potassium dicyanoargentate (I) (AlfaAesar 12551)  
Potassium dicyanoaurate (I) (AlfaAesar 12552)  
Potassium ferrocyanide (II) trihydrate (Aldrich 22,768-4)  
Potassium hexacyanocobaltate (III) (AlfaAesar 23126)  
Potassium tetracyanonickelate (II) hydrate  
(Strem 93-2836)  
Sodium cyanide, 99.99% (Aldrich 43,159-1)  
Sodium hydroxide solution 50% w/w (Fisher SS254)  
Sodium perchlorate monohydrate, HPLC-grade  
(Fisher S490)

### 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 M $\Omega$ -cm or greater. Filter the water through a 0.2- $\mu$ m 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>]<sub>n</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.

### 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

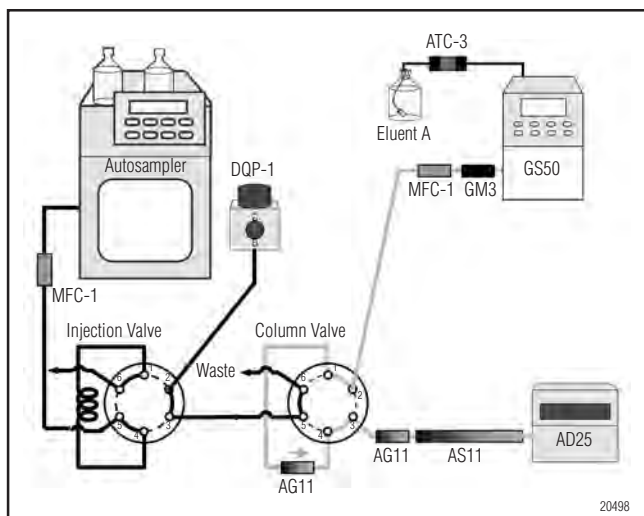
**Table 2. Metal Cyanide Calibration Standards**

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

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 GS50 pump flow rate is within specifications and recalibrate if necessary. A GS50 should deliver water at 1.0 ± 0.005 mL/min against a constant backpressure of 2000 psi. The DQP-1 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 DQP-1 and MFC-1 trap column, before the column valve. Adjust the length of the tubing to provide 100–200 psi of backpressure. Then adjust the DQP-1 pump to deliver a flow rate of 1 mL/min against the backpressure that results during the preconcentration step. The DQP-1 should be left on continuously during a day's run; refill the reagent water reservoir as needed. Verify that the 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 AD25 reference cell current and the UV lamp's elapsed time. This information may prove useful for troubleshooting.

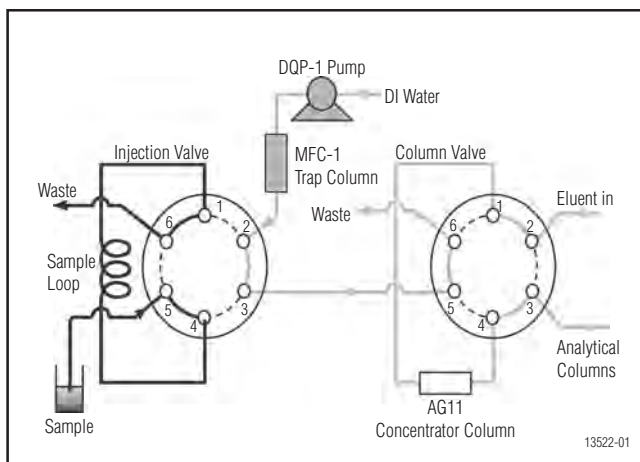


**Figure 1.** Diagram of the system used for determination of metal cyanide complexes by IC with on-line sample preconcentration.

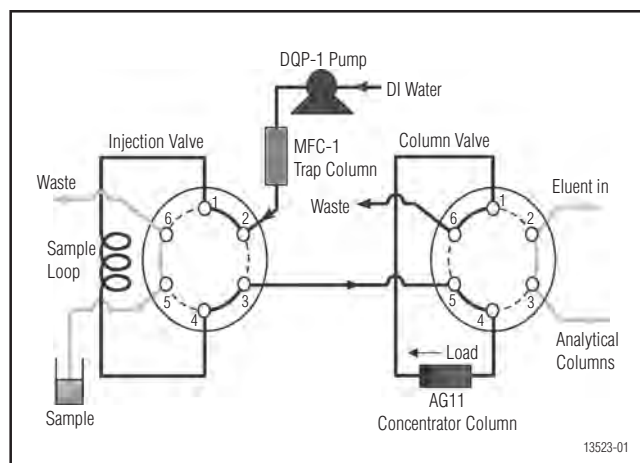
Prepare the eluents and set up the system as depicted in Figure 1. Using this system, the AS50 uses 8 mL of sample to flush and fill the 5-mL sample loop. At Time = 0, the inject valve moves to the inject position, allowing the DQP-1 pump to preconcentrate the 5 mL of sample onto the AG11 concentrator 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 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.

Install an IonPac ATC-3 between eluent reservoir A and the pump inlet. The ATC-3 removes metal cyanide impurities present in the sodium cyanide solution that would otherwise cause elevated background noise. Regenerate the ATC-3 as needed by using a Trap Column/Suppressor Cleanup Kit (P/N 059659) according to the installation and instruction manual (Document No. 031835)

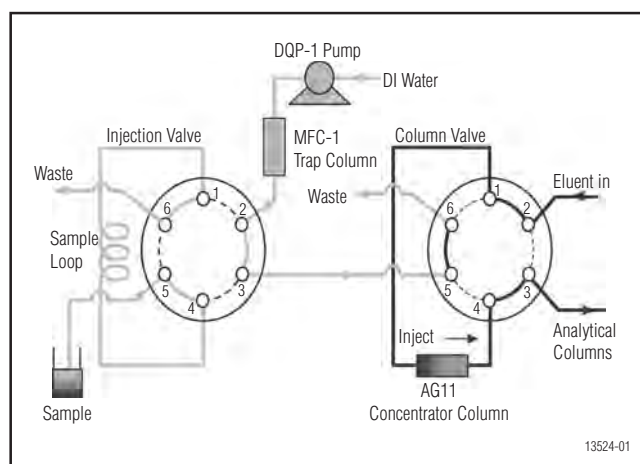
Install and configure the autosampler with the AS50 dual-valve needle assembly (P/N 061267). Install a 10-mL sample syringe and enter a “Sample Syringe Volume” of 1 mL in the AS50 Plumbing Configuration Screen. Install a 5-mL sample loop between ports 1 and 4 of the injection valve and enter a “Sample Loop Size” of 200  $\mu$ L in the AS50 Plumbing Configuration Screen.



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



**Figure 3.** Schematic of an IC system during preconcentration of the sample on the AG11 column.



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



**Table 3. Linear Ranges and MDLs for Metal Cyanide Complexes**

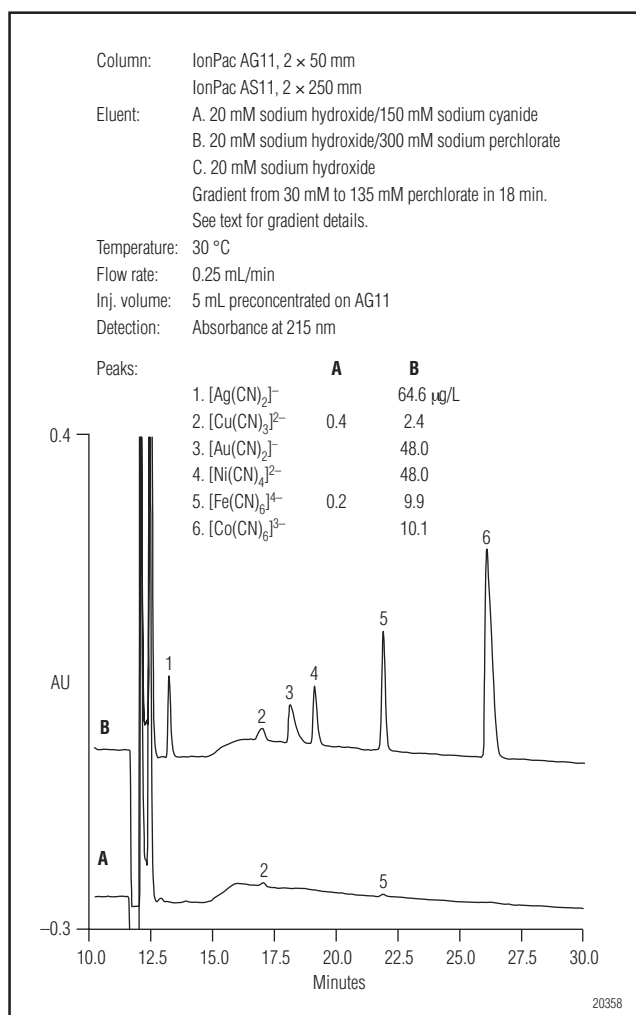
Analyte	Range (µg/L)	MDL Standard (µg/L)	r <sup>2</sup>	MDL* (µg/L)
[Ag(CN) <sub>2</sub> ] <sup>-</sup>	8–125	15	0.99611	1.08
[Au(CN) <sub>2</sub> ] <sup>-</sup>	6–100	10	0.99931	1.92
[Cu(CN) <sub>3</sub> ] <sup>2-</sup>	0.3–5	0.8	0.98538	0.41
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	6–100	50	0.99523	4.11
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	1–20	1.0	0.99995	0.17
[Co(CN) <sub>6</sub> ] <sup>3-</sup>	12–200	10	0.99999	2.20

\* 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.

When setting up the sequence, enter an “Injection Volume” of 200 µL. The AS50 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 AG11 preconcentrator column between ports 1 and 4 of the column valve. Refer to the operator’s manual for the AutoSelect AS50 (Document No. 31169) and the AS50 large-volume sampling needle assembly instructions for details.

Install a 2 × 50 mm IonPac AG11 and 2 × 250 mm 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.

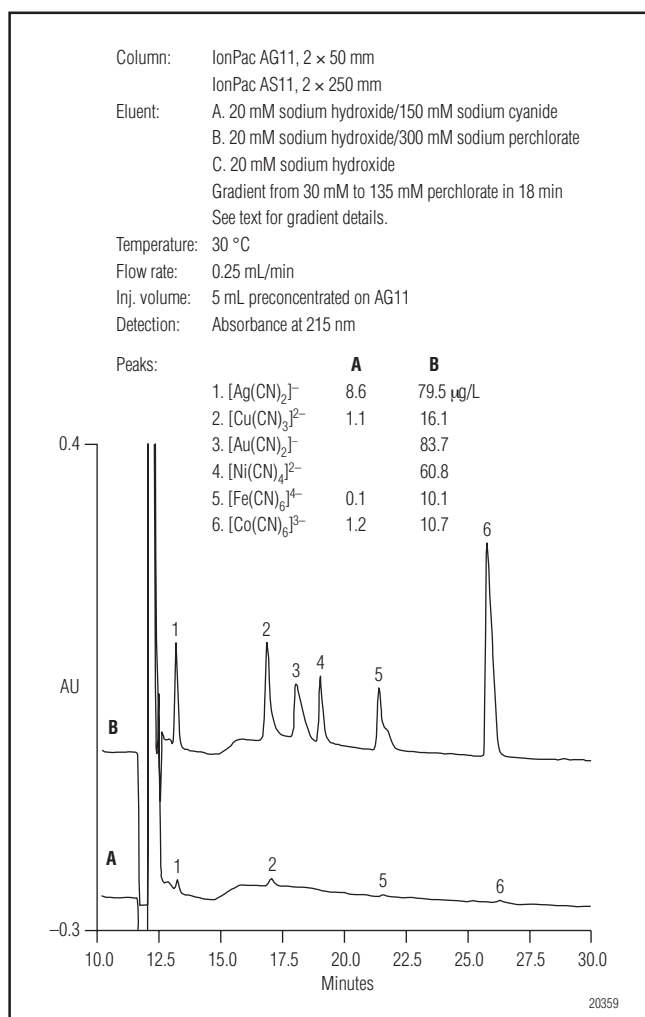
Inject a mid-level standard, such as the Level 2 standard in Table 2. The column is equilibrated when two consecutive injections of the standard produce the same retention time for the metal cyanide complex anions. Confirm that the resulting chromatogram resembles the chromatogram of the standard shown in Figure 5B.



**Figure 5.** Anion-exchange separation with preconcentration 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).

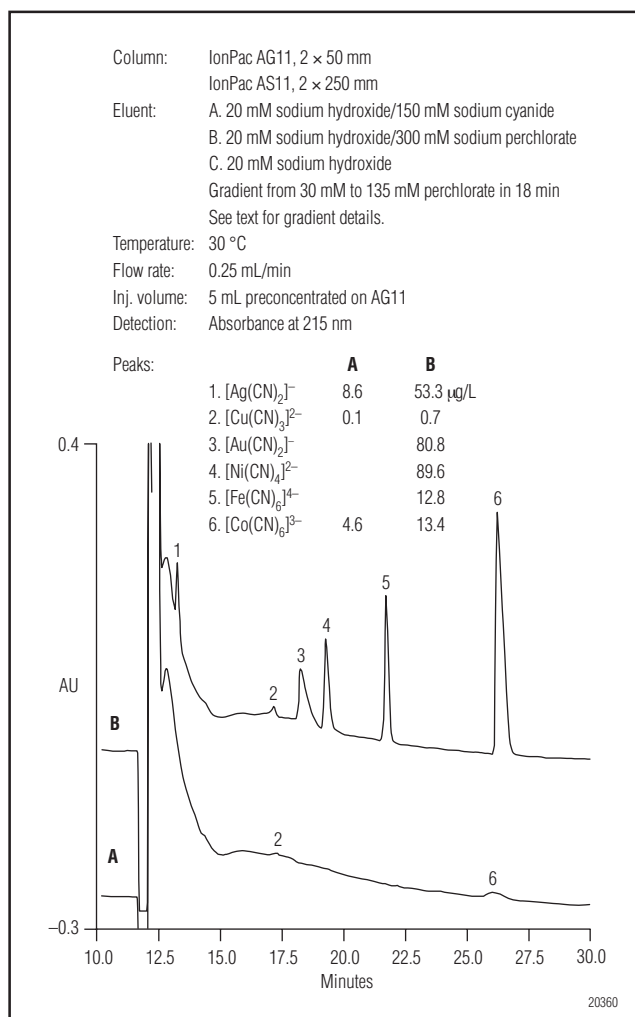
## RESULTS AND DISCUSSION

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 AS11, 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.



**Figure 6.** Anion-exchange separation with preconcentration 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.

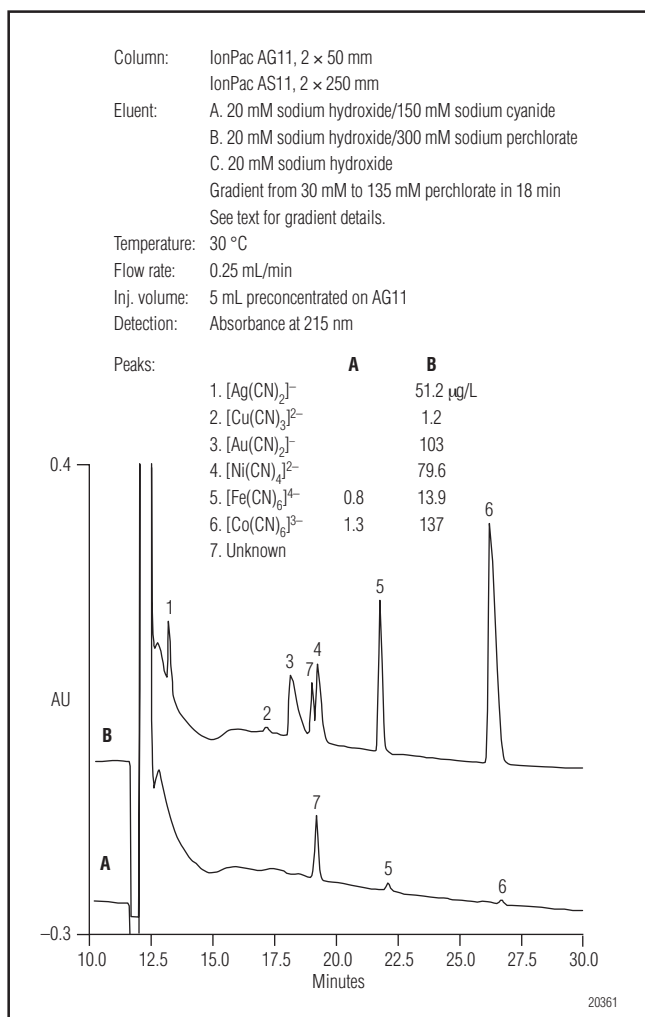
To determine method detection limits (MDLs) for this method, make seven injections of reagent water fortified with metal cyanide complexes at concentrations yielding peaks approximately five times higher than the background noise. In column 3 of Table 1, we list the concentrations of six metal cyanides 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-µg/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



**Figure 7.** Anion-exchange separation with preconcentration 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.

concentrations analyzed in this application note, a small interfering peak was observed to coelute with copper cyanide [Cu(CN)<sub>3</sub>]<sup>2-</sup>. This interferent increases the MDL for copper cyanide. Careful attention to regenerating the 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 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.

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 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.

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

**Table 4. Recovery of Metal Cyanide Complexes from Environmental Waters**

Anion	% Recovery				
	Deionized Water	Drinking Water	Surface Water	Ground-water	Waste-water
[Ag(CN) <sub>2</sub> ] <sup>-</sup>	63.6	82.3	54.3	51.1	30.84
[Au(CN) <sub>2</sub> ] <sup>-</sup>	107	110	82.4	120	92.6
[Cu(CN) <sub>3</sub> ] <sup>2-</sup>	121	408	41.9	18.0	38.0
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	99.4	76.3	88.2	104	2.52
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	101	99.9	100	99.5	97.2
[Co(CN) <sub>6</sub> ] <sup>3-</sup>	99.0	105	105	100	99.9

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 [Fe(CN)<sub>6</sub>]<sup>4-</sup>. Calibration is based on the iron (II) cyanide complex. Report results as mg/L of [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> so as to represent the sum of ferrocyanide and ferricyanide. If unreduced [Fe(CN)<sub>6</sub>]<sup>3-</sup> 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 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 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 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.

### CONCLUSION

This method of on-line preconcentration allows determination of metal cyanide complexes at  $\mu\text{g/L}$  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-AWWA-WPCF. 4500-CN B., pp 4–34.
2. *Ibid*, p 38.
3. *Ibid*, p 28.
4. Dionex Corporation. Application Update 147; Sunnyvale, CA.
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-AWWA-WPCF. 4500-CN B., pp 4–25.

### LIST OF SUPPLIERS

Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, P.O. Box 355, Milwaukee, WI 53233 USA, Tel: 800-558-9160, [www.aldrich.sial.com](http://www.aldrich.sial.com).

Alfa Aesar, 30 Bond St., Ward Hill, MA 01835 USA, Tel: 800-343-0660, [www.alfa.com](http://www.alfa.com).

Fisher Scientific, 2000 Park Lane, Pittsburgh, PA 15275-1126 USA, Tel: 800-766-7000, [www.fishersci.com](http://www.fishersci.com).

Strem Chemical, 7 Mulliken Way, Newburyport, MA 01950-4098 USA, Tel.: 1-800-647-8736, [www.strem.com](http://www.strem.com).

VWR Scientific Products, 1310 Goshen Parkway, West Chester, PA 19380 USA, Tel: 800-932-5000, [www.vwr.com](http://www.vwr.com).



IonPac and Chromleon are registered trademark of Dionex Corporation.  
Acrodisk is a registered trademark of Gelman Corporation.

**Dionex Corporation**  
1228 Titan Way  
P.O. Box 3603  
Sunnyvale, CA  
94088-3603  
(408) 737-0700

**Dionex Corporation**  
Salt Lake City Technical Center  
1515 West 2200 South, Suite A  
Salt Lake City, UT  
84119-1484  
(801) 972-9292

**Dionex U.S. Regional Offices**  
Sunnyvale, CA (408) 737-8522  
Westmont, IL (630) 789-3660  
Houston, TX (281) 847-5652  
Atlanta, GA (770) 432-8100  
Marlton, NJ (856) 596-06009

**Dionex International Subsidiaries**  
*Australia* 61 (2) 9420 5233 *Austria* (01) 616 51 25 *Belgium* (03) 353 42 94 *Canada* (905) 844-9650 *China* (852) 2428 3282  
*Denmark* 36 36 90 90 *France* 01 39 30 01 10 *Germany* 06126-991-0 *Italy* (06) 66 51 50 52 *Japan* (06) 6885-1213 *Korea* 82 2 2653 2580  
*The Netherlands* (0161) 43 43 03 *Switzerland* (062) 205 99 66 *United Kingdom* (01276) 691722  
\* Designed, developed, and manufactured under an NSAI registered ISO 9001 Quality System.

