

Determination of Metal Cyanides

INTRODUCTION

Transition metal cyanides typically exist in solution as the anionic cyanometallates, $M(CN)_x^{n-}$. Since these complexes are very stable (formation constants being as high as 10^{35} for $Fe(CN)_6^{4-}$), they may be separated by anion exchange chromatography.

Cyano complexes of most of the transition metals absorb low-wavelength ultraviolet light, making detection at ≈ 215 nm a convenient method for determination.

STANDARDS

The standards for this method should be sodium or potassium salts of the cyanometallates. The table below lists available potassium salts as well as possible suppliers and amounts necessary to prepare 100 mL aqueous standards with metal concentrations of 1000 ppm. No cyanocuprate is available, although copper(I) cyanide ($CuCN$) will slowly dissolve in water containing sodium cyanide. Atomic absorption standards are not recommended for use as cyanometallate standards.

Reagent	Mass per 100 mL Solution	Supplier
$KAg(CN)_2$	0.185 gram	Aesar (800-343-1990)
$KAu(CN)_2$	0.146	Aesar
$CuCN$	0.136*	Alfa (800-343-0660)
$K_2Ni(CN)_4$	0.411	Strem (617-462-3191)
$K_4Fe(CN)_6 \cdot 3H_2O$	0.756	Alfa
$K_2Pd(CN)_4 \cdot 3H_2O$	0.322	Alfa
$K_3Co(CN)_6$	0.564	Alfa
$K_2Pt(CN)_4 \cdot 3H_2O$	0.221	Aesar

*Dissolve the $CuCN$ with 0.300 g sodium cyanide in 50 mL of water, then dilute the solution to 100 mL. All other reagents should be dissolved in water and diluted to 100 mL.

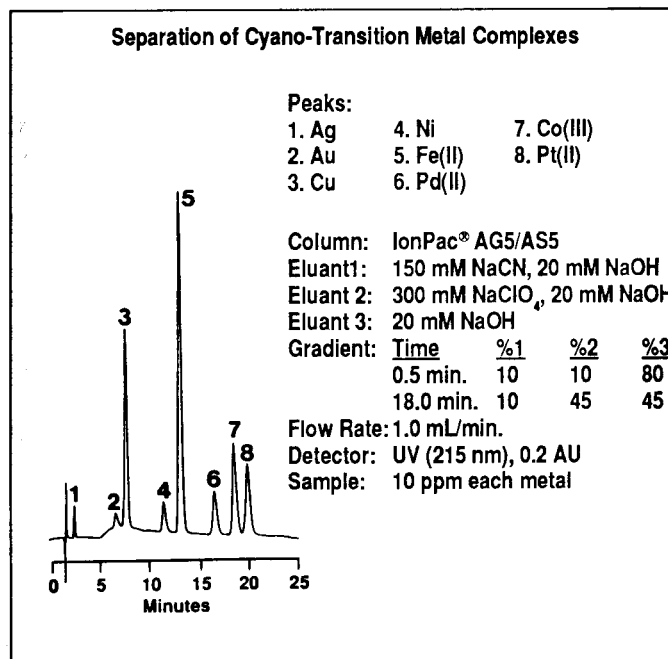


Figure 1

ANALYTES

$Ag(CN)_2^-$, $Au(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Pd(CN)_4^{2-}$, $Co(CN)_6^{3-}$ and $Pt(CN)_4^{2-}$.

DISCUSSION OF METHOD

The anionic cyanometallates are separated on the IonPac® AS5 column using an 18-minute gradient of 30 to 135 mM perchlorate (Figure 1). Hydroxide and cyanide concentrations are constant at 20 mM and 15 mM, respectively, and are present to maintain the integrity of the complexes.

Form of metal anion The silver, gold, copper and nickel peaks are measures of total metal. Silver is present as $Ag(I)(CN)_2^-$. If present, $Cu(II)$ would be reduced to $Cu(I)$ under the chromatographic conditions. $Au(I)(CN)_2^-$ and $Au(III)(CN)_4^-$ display identical chromatograms, so one is probably converted to the other. The cyanocuprate ion behaves as the dianion, $Cu(CN)_3^{2-}$. Nickel is present as $Ni(II)(CN)_4^{2-}$.

Fe(III)(CN)₆³⁻ is slowly reduced to Fe(II)(CN)₆⁴⁻ by the high pH of metal cyanide samples, hence iron will usually be in the reduced form exclusively. Fe(III)(CN)₆³⁻, if present, elutes as a tail of the Fe(II) peak.

Cobalt, on the other hand, is present in the oxidized form in fresh samples and remains as Co(III)(CN)₆³⁻ for months before slowly reducing to a Co(II) complex. Pd(II)(CN)₄²⁻ and Pt(II)(CN)₄²⁻ are very inert dianions, which do not interconvert with the more oxidized Pd(IV)(CN)₆²⁻ and Pt(IV)(CN)₆²⁻. Furthermore, the Pd(IV) and Pt(IV) complexes do not strongly absorb ultraviolet light so they cannot be detected by this method.

It is possible to alter the gradient to suit individual requirements. For example, if better separation of Ag, Au and Cu is needed, starting with weaker perchlorate or delaying the start of the gradient will accomplish that. If only strongly retained complexes such as Pd or Pt are of interest, isocratic conditions at about 120 mM perchlorate may be more desirable. In any case, it is important to elute all complexes after each analysis to avoid loss of column capacity. This will usually involve a gradient to remove Fe and Co. The standard injection loop size is 50 µL; however, injections of 500 µL may be made with equal success.

RECOMMENDED EQUIPMENT

Dionex Series 4500i or 4000i Ion Chromatograph with a VDM-I, VDM-II or UDM.

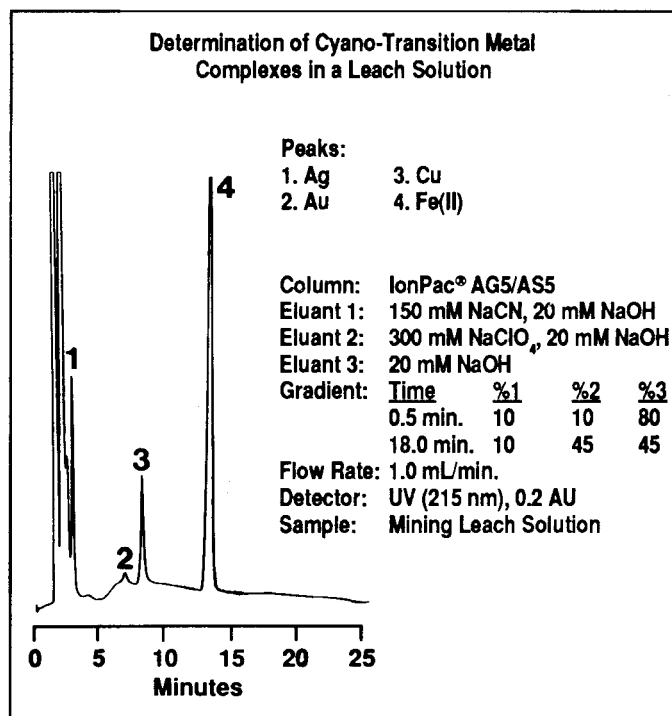


Figure 2

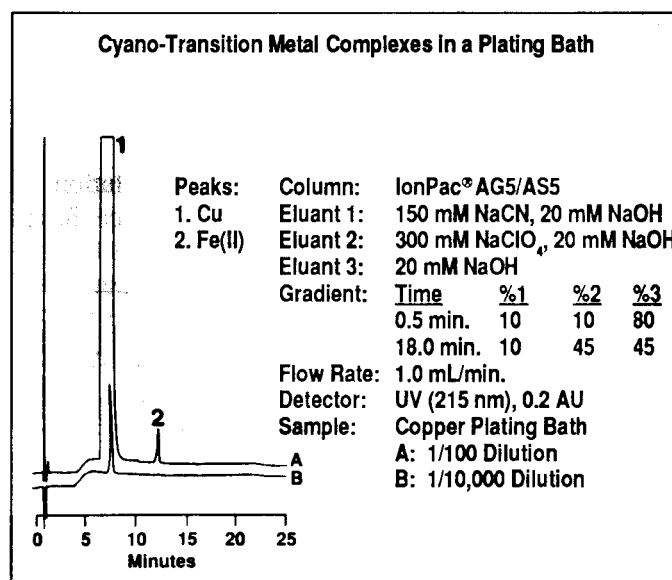


Figure 3

PRECAUTIONS

It is recommended that gloves be worn when working with any cyanide. Under no circumstance should acid contact cyanide; this would generate hydrogen cyanide gas, an extremely toxic substance. All work should be done in a well-ventilated area. It is advisable to add sodium hypochlorite (household bleach) to the eluant waste container in order to destroy cyanide.

CONDITIONS

Sample Loop Volume: 50 µL
Guard Column: IonPac AG5
Separator Column: IonPac AS5
Eluant 1: 20 mM NaOH, 150 mM NaCN
Eluant 2: 20 mM NaOH, 300 mM NaClO₄
Eluant 3: 20 mM NaOH
Eluant Purifier (Eluant 1): 1.0 cm × 10 cm low pressure column body filled with Bio-Rad® AG®2-X8 or equivalent

Flow Rate: 1.0 mL/min.
Expected Pressure: 700–900 psi
Detector Wavelength: 215 nm

Gradient Program:

Time min.	Eluant 1	Eluant 2	Eluant 3
0.0	10%	10%	80%
0.5	10	10	80
18.0	10	45	45

Reset the GPM to initial conditions after the analysis is complete. Hold at initial conditions for 10 minutes before the next injection is made.

SOLUTIONS AND REAGENTS

Eluant 1: 20 mM NaOH, 150 mM NaCN
Dilute 1.6 g of sodium hydroxide solution (50%, low carbonate) and dissolve 7.35 g of sodium cyanide (ACS reagent grade) in enough 18 M-ohm deionized water to make 1.0 L of solution.

Eluant 2: 20 mM NaOH, 300 mM NaCN
Dilute 1.6 g of sodium hydroxide solution (50%, low carbonate) and dissolve 36.7 g of sodium perchlorate (Fisher HPLC grade) in enough 18 M-ohm deionized water to make 1.0 L of solution.

Eluant 3: 20 mM NaOH
Dilute 1.6 g of sodium hydroxide solution (50%, low carbonate) in enough 18 M-ohm deionized water to make 1.0 L of solution.

Commercial sodium cyanide contains some cyanometallate impurities which interfere with the analysis. These may be removed by placing a low pressure anion exchange column between Eluant 1 and the GPM. Use the Iron Guard Column Kit (P/N 042021) filled with a high-capacity anion exchange resin (Bio-Rad AG2-X8 or equivalent). After filling the column casing with dry resin (ca 6 g), the resin is conditioned by passing 400 mL of 500 mM NaOH followed by 300 mL of Eluant 1 through the column. A column conditioned in this manner will purify at least 3 L of Eluant 1.

SAMPLE PREPARATION

This analytical method is most suited to alkaline samples containing excess cyanide, e.g., mining and metal finishing samples. Often, the samples need only be filtered through a 1.0 μ or smaller filter. If high concentrations of metals are present, the sample may have to be diluted with deionized (18 M-ohm) water. No further pretreatment of the sample should be necessary. Figures 2 and 3 are typical sample chromatograms.

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