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DETERMINATION OF METAL–CYANO COMPLEXES BY REVERSED-PHASE ION-INTERACTION HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY AND ITS APPLICATION TO THE ANALYSIS OF PRECIOUS METALS IN GOLD PROCESSING SOLUTIONS

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SUMMARY

A chromatographic procedure is described for the separation of metal–cyano complexes using reversed-phase ion-interaction high-performance liquid chromatography. Cyano complexes of copper(I), silver(I), iron(II), cobalt(III), iron(III), gold(I), palladium(II) and platinum(II) may be resolved on a C_{18} column using a mobile phase of acetonitrile–water (23:77, v/v) containing 0.005 M tetramethylammonium hydroxide, with UV detection at 214 nm. Alternatively, cyano complexes of cobalt(III), copper(I), silver(I), nickel(II), palladium(II), gold(I) and platinum(II) may be resolved on a cyano column using a mobile phase of acetonitrile–water (8:92, v/v) containing 0.005 M tetramethylammonium hydroxide. The influence of variation of the nature of the ion-interaction reagent is discussed.

The method is applied to the analysis of gold in processing solutions taken from the carbon-in-pulp process and excellent agreement between the chromatographic method and inductively coupled plasma atomic emission spectroscopic analysis is reported. Detection limits for precious metals were 1.9, 2.6, 0.9 and 0.8 ng for silver(I), gold(I), platinum(II) and palladium(II), respectively. Precision of the method for gold at the 0.1-μg level was 1.00% for peak area measurements and the calibration plot for gold was linear for injections containing up to 0.3 μg of gold.

INTRODUCTION

Two main approaches to the determination of metal ions by liquid chromatography may be identified. The first is the formation of metal chelates through pre-column derivatisation reactions with subsequent separation of these chelates by normal- or reversed-phase chromatography, and the second approach is the use of ion-exchange chromatography.

In the metal–chelate method, the ligand chosen is usually a widely reactive species capable of forming very stable complexes which have suitably high molar extinction coefficients in order to facilitate sensitive detection. Typical ligands are

diethyldithiocarbamate[1,2], β-diketones[3] and dithizone[4], and the method proves most useful for the separation of transition metal ions. On the other hand, modern ion-exchange methods are more widely applicable and generally employ an eluent containing a competing cation and a complexing ligand, so that separation is based on a combination of ion-exchange selectivity and complexation characteristics[5].

In recent years, the rising value of precious metals has aroused considerable interest in the trace determination of these species and this has led to the development of spectroscopic methods of analysis using such techniques as atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic emission spectroscopy (ICPAES). The main disadvantages of these methods are their inability to differentiate between oxidation states of the same element and the occurrence of spectral interferences. Chromatographic techniques do not suffer from these disadvantages and are therefore especially attractive for precious metal analysis. In practice however, neither of the above-mentioned chromatographic approaches has been widely applied to the determination of precious metals although a number of classical open-column methods have been reported. These methods involve the conversion of precious metals to their anionic chloro complexes, with separation on an anion-exchange column using hydrochloric acid (up to 12 M) as eluent[6,7]. Under these conditions, the gold(I) tetrachloro complex is strongly adsorbed unless an organic solvent such as methanol is added to the eluent[7]. This classical method has been adapted for use on modern ion chromatography columns by Rocklin[8] who successfully separated platinum from either palladium or gold as their chloro complexes using an eluent containing 0.3 M perchlorate and 0.05 M hydrochloric acid. The corrosive nature of this eluent necessitated the use of a chromatographic system in which non-metallic components were employed wherever contact with the eluent was required.

In this paper, we describe the separation of metal ions after conversion to their cyano complexes. Cyanide is shown to be a useful ligand in that it forms stable complexes with a wide range of metal ions, including the precious metals, and these complexes may be conveniently separated by reversed-phase ion-interaction chromatography using non-corrosive eluents. This approach is successfully applied to the analysis of precious metals in gold processing solutions.

EXPERIMENTAL

Instrumentation

The liquid chromatograph used consisted of a Waters Assoc. (Milford, MA, U.S.A.) M6000 pump, a Model U6K injector, a Model 441 absorbance detector operated at 214 nm and a Houston Instruments (Austin, TX, U.S.A.) Ominiscribe recorder. For quantitative analysis, the recorder was replaced with a Waters Assoc. M730 data module.

Two columns were used in this study: a Waters Assoc. Nova Pak C_{18} column and a Waters Assoc. Nova Pak Cyano column. Both columns were packed with 5-μm particles and were of the same dimensions (150 $\times$ 3.9 mm I.D.).

Spectroscopic analyses for gold were performed using a Labtam International (Melbourne, Australia) inductively coupled plasma atomic emission spectrometer operated at 242.8 nm.

Reagents and procedures

Potassium ferrocyanide (By-Products and Chemicals, Sydney, Australia), potassium ferricyanide (Hopkin and Williams, London, U.K.) and potassium dicyanoaurate(I) (Johnson and Matthey Chemicals, London, U.K.) were purchased as pure compounds. Potassium salts of tetracyanozincate(II), tetracyanocadmate(II), tetracyanomercurate(II), tetracyanonickelate(II), tetracyanocuprate(I), hexacyanomanganate(III), hexacyanochromate(III), tetracyanopalladate(II), tetracyanoplatinate(II) and dicyanoargentate(I) were synthesised using previously published procedures[9,10]. The compositions of these substances were verified using microanalysis and ICPAES. All cyano complexes were stored in a vacuum desiccator in the absence of light. Standard solutions of individual complexes and mixtures were prepared by dissolving weighed amounts of the complexes in a 100-ppm solution of alkaline potassium cyanide. Standard solutions were stored in the absence of light.

Methanol used was analytical reagent grade (May and Baker, Sydney, Australia) and was doubly distilled in an all-glass apparatus. Waters Assoc. chromatographic grade acetonitrile (UV cut-off 190 nm) was used and all water for the preparation of mobile phases was purified by passage through a Millipore (Bedford, MA, U.S.A.) Milli Q water purification system. Mobile phases were prepared by diluting the appropriate volume of organic modifier with water, adding tetramethylammonium hydroxide or tetrabutylammonium phosphate (Waters Assoc. low UV PIC A or PIC A, respectively) to give a final concentration of 0.005 M and diluting to volume. The mobile phase was then filtered through a 0.45-μm membrane filter and degassed in an ultrasonic bath before use.

All chromatographic separations were carried out at room temperature, using a mobile phase flow-rate of 1.0 ml/min.

RESULTS AND DISCUSSION

Properties of metal cyano complexes

Table I lists some of the properties of metal–cyano complexes which are of importance to a study of their determination by chromatographic methods. It can be seen from Table I that all complexes possess relatively high stability constants and that the number of cyano ligands bound to the central metal ion varies from two to six. This factor should contribute to selectivity effects and hence assist in the separation of these complexes. Table I also shows that the majority of the complexes are detectable by UV absorption at 214 nm.

Chromatographic behaviour of metal–cyano complexes

The ionic nature of the cyano complexes suggested that ion-exchange or ion-interaction chromatography could be suitable for their separation. Initial studies with low capacity anion-exchange columns resulted in poor separations and required the use of corrosive and toxic eluents. Attention was therefore directed at ion-interaction methods and a systematic study of column type, nature and concentration of the organic modifier, and nature of the ion-interaction reagent was undertaken.

Initial studies with the C_{18} Nova Pak column, using methanol as organic modifier and tetramethylammonium hydroxide as the ion-interaction reagent showed that suitable chromatographic peaks were obtained for all complexes except for zinc(II),

TABLE I

STABILITY AND UV ABSORPTION DATA FOR METAL–CYANO COMPLEXES

Stability data taken from refs. 10 and 11.

Metal ion	Complex	Overall formation constant, $\log \beta$	Wavelength of maximum absorption* (nm)
Ag^+	$Ag(CN)_2^-$	21.1	202
Au^+	$Au(CN)_2^-$	38.3	211
Cu^+	$Cu(CN)_4^{3-}$	30.3	206
Cd^{2+}	$Cd(CN)_4^{2-}$	18.9	205
Hg^{2+}	$Hg(CN)_4^{2-}$	41.5	200
Ni^{2+}	$Ni(CN)_4^{2-}$	31.3	201
Pd^{2+}	$Pd(CN)_4^{2-}$	42.4	212
Pt^{2+}	$Pt(CN)_4^{2-}$	41.0	215
Zn^{2+}	$Zn(CN)_4^{2-}$	16.7	208
Co^{2+}	$Co(CN)_6^{3-}$	64.0	203
Cr^{3+}	$Cr(CN)_6^{3-}$	–**	199
Fe^{2+}	$Fe(CN)_6^{4-}$	35.4	215
Fe^{3+}	$Fe(CN)_6^{3-}$	43.6	204
Mn^{3+}	$Mn(CN)_6^{3-}$	9.7	–***

    * Absorption spectra were measured by dissolving the complexes in an aqueous solution containing 100 ppm cyanide, and with the same concentration of cyanide as the reference solution.
    ** No value available.
    *** Complex was unstable in 100 ppm cyanide solution.

which was only weakly absorbing at the wavelength used, and mercury(II), which gave poor peak shape. In addition, tetracyanocadmate(II) showed no retention and hexacyanomanganate (III) was found to be unstable in solution, forming a brown precipitate (presumably manganese dioxide) after storage for a short period. The four abovementioned complexes were not studied further.

TABLE II

RETENTION TIMES (min) FOR METAL–CYANO COMPLEXES ON THE NOVA PAK C_{18} COLUMN

Conditions: mobile phase contains the stated percentage (v/v) of acetonitrile and 0.005 M tetramethylammonium hydroxide. A flow-rate of 1.0 ml/min was used.

Metal complex	Amount of acetonitrile in mobile phase (%)			
	20	23	25	30
$Cu(CN)_4^{3-}$	7.3	5.3	4.5	3.5
$Ag(CN)_2^-$	8.5	6.3	5.7	4.5
$Fe(CN)_6^{4-}$	15.0	10.8	9.4	5.8
$Co(CN)_6^{3-}$	21.8	15.0	8.4	4.8
$Fe(CN)_6^{3-}$	25.0	17.8	10.0	5.2
$Ni(CN)_4^{2-}$	27.9	15.9	8.9	5.4
$Au(CN)_2^-$	35.4	26.0	18.4	12.6
$Cr(CN)_6^{3-}$	39.7	30.9	16.2	10.2
$Pd(CN)_4^{2-}$	44.8	28.8	18.0	11.2
$Pt(CN)_4^{2-}$	51.5	33.3	20.1	14.5

TABLE III

RETENTION TIMES (MIN) FOR METAL-CYANO COMPLEXES ON THE NOVA PAK CN COLUMN

Conditions as for Table II.

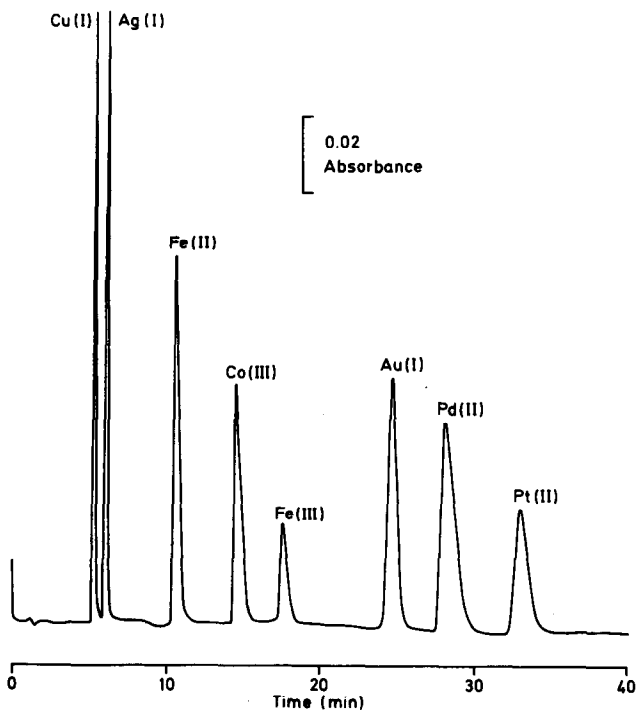| Metal complex	Amount of acetonitrile in the mobile phase (%)				
	5	8	10	13	15
$Fe(CN)_6^{4-}$	1.6	1.6	1.6	1.6	1.6
$Co(CN)_6^{3-}$	3.2	2.3	1.8	1.8	1.6
$Fe(CN)_6^{3-}$	3.2	2.3	1.8	1.8	1.6
$Cu(CN)_4^{3-}$	3.8	3.1	2.4	2.2	2.2
$Cr(CN)_6^{3-}$	5.2	4.0	2.0	2.0	2.0
$Ag(CN)_2^{-}$	5.3	4.2	3.7	3.2	3.2
$Ni(CN)_4^{2-}$	13.4	7.7	5.2	4.0	3.8
$Pd(CN)_4^{2-}$	25.2	17.2	9.8	7.4	6.2
$Au(CN)_2^{-}$	29.4	21.4	15.4	12.6	11.6
$Pt(CN)_4^{2-}$	42.8	23.4	12.6	9.0	7.2

Fig. 1. Separation of metal–cyano complexes on a C_{18} column. Conditions: column, Waters Assoc. Nova Pak C_{18}, 150 × 3.9 mm I.D.; eluent, acetonitrile–water (23:77, v/v) containing 0.005 M tetramethylammonium hydroxide; flow-rate, 1.0 ml/min; sample, 10 μl of a solution containing 0.15 μg Cu(I), 1.5 μg Ag(I), 0.02 μg Fe(II), 0.2 μg Co(III), 0.3 μg Fe(III), 2.0 μg Au(I), 0.4 μg Pd(II) and and 0.2 μg Pt(II); detection, UV absorption at 214 nm.
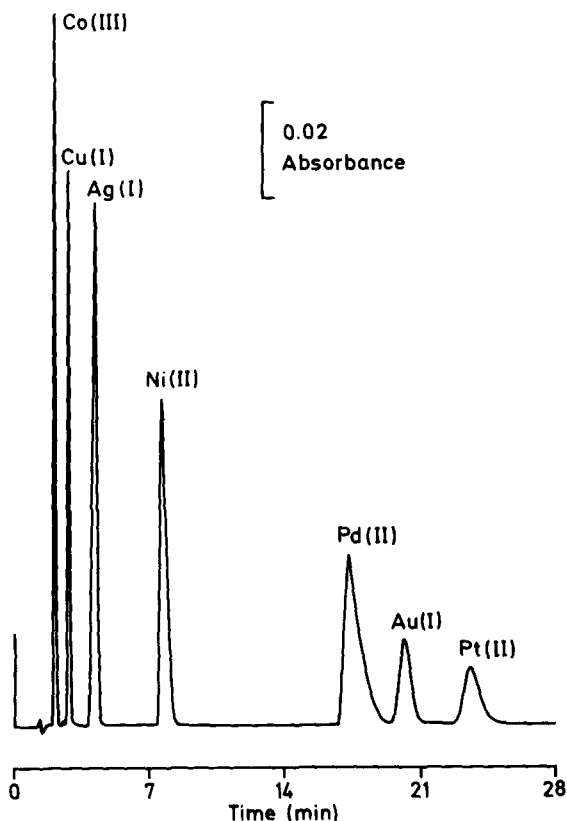
Fig. 2. Separation of metal–cyano complexes on a CN column. Conditions: column, Waters Assoc. Nova Pak CN, 150 × 3.9 mm I.D.; eluent, acetonitrile–water (8:92, v/v) containing 0.005 M tetramethyl-ammonium hydroxide; sample, 10 μl of a solution containing 0.2 μg Co(III), 0.15 μg Cu(I), 1.0 μg Ag(I), 0.8 μg Ni(II), 0.25 μg Pd(II), 0.5 μg Au(I) and 0.08 μg Pt(II). Other conditions as for Fig. 1.

Peaks obtained with methanol as the organic modifier were unusually broad, leading to poor resolution of the eluted complexes. However, when acetonitrile was used at the same eluotropic strength, peak shape dramatically improved and aceto-nitrile was therefore used in all subsequent analyses.

Retention data were obtained for the C_{18} and Cyano Nova Pak columns, using tetramethylammonium hydroxide as the ion-interaction reagent and acetonitrile as the organic modifier. These data are presented in Tables II and III, respectively, and representative chromatograms for each column type are given in Figs. 1 and 2.

The C_{18} column provided separation of up to eight metal complexes (Fig. 1), with the precious metal complexes (except for silver) eluting towards the end of the chromatogram. Some mutual interference was observed between the complexes of nickel(II), cobalt(III) and iron(III), and also between those of chromium(III) and platinum(II), however resolution of these species was possible at the expense of lengthy analysis times. It is noteworthy that very small changes in the percentage of acetonitrile in the mobile phase produced relatively large changes in retention times, indicating that the mobile phases should be prepared with care.

Significant changes in retention and selectivity were observed when the cyano column was used (Fig. 2). The complexes were less strongly retained and the elution order differed from that obtained on the C_{18} column: in particular, the hexacyano species [that is, iron(II), iron(III), cobalt(III) and chromium(III)] all eluted very early and were essentially unresolved. This effect can be attributed to the steric differences between the octadecyl and cyanopropyl functionalities present in the two columns. The elution order of the palladium(II) and gold(I) complexes also differed between the two columns.

The effect of changing the nature of the ion-interaction reagent was examined by substituting tetrabutylammonium phosphate for the tetramethylammonium hydroxide reagent used to obtain the data shown in Tables II and III. On the C_{18} column, an overall increase in retention of the cyano complexes was observed, which is the expected result when the hydrophobicity of the ion-interaction reagent is increased, leading to an increase in adsorption of the reagent onto the column surface[12]. On the other hand, the cyano column showed the opposite behaviour, with significant decreases in retention times occurring with the tetrabutylammonium reagent. This effect is illustrated in Fig. 3 which was obtained under the same conditions
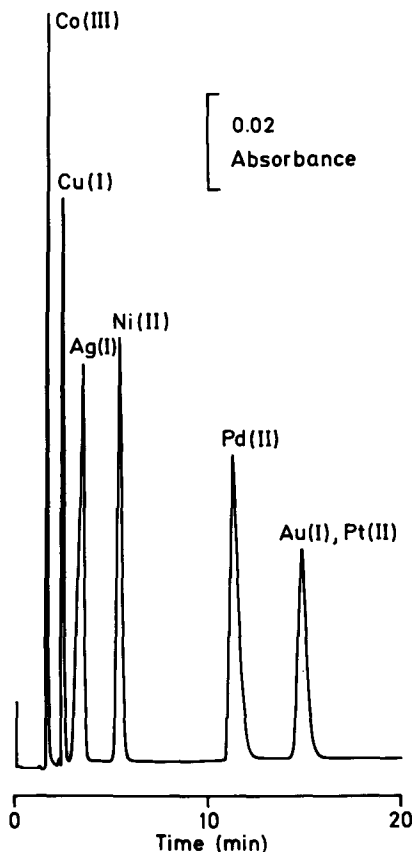

Fig. 3. Effect of variation of the nature of the ion-interaction reagent. Conditions as for Fig. 2, except that 0.005 M tetrabutylammonium phosphate was used as the ion-interaction reagent in the mobile phase.

as those used for Fig. 2, except for the ion-interaction reagent used. The coelution of the cyano complexes of gold(I) and platinum(II) shown in Fig. 3 suggested that the tetrabutylammonium reagent was unsuitable for the determination of precious metals.

Analysis of gold processing solutions

The extraction of gold and silver from ores is accomplished almost exclusively by cyanidation, which involves leaching the crushed ore with an alkaline solution of sodium or potassium cyanide. In this process, precious metals as well as a number of base metals are converted to their soluble cyano complexes. Gold is recovered from this leach solution either by zinc dust precipitation or the carbon-in-pulp (CIP) adsorption process[13-15]. In the CIP method, the gold(I)–cyano complex is concentrated by counter-current adsorption onto activated charcoal and is then displaced, collected and refined. Monitoring of the concentration of gold (and other precious metals) at various stages of the leaching and adsorption steps in the CIP process requires an analytical method which provides reliable results over the concentration
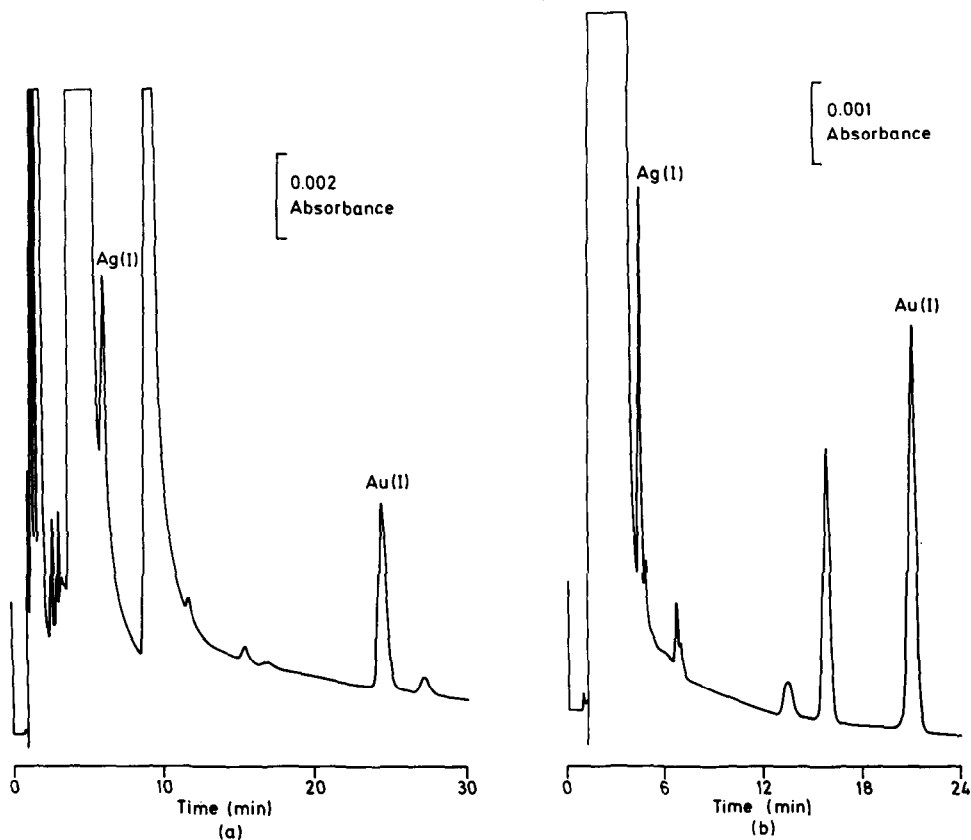

Fig. 4. Chromatographic analysis on a C_{18} column (a) and a CN column (b) of a leach solution taken from a carbon-in-pulp gold processing plant. Conditions: injection volume, 50 μl; (a) other conditions as for Fig. 1, and (b) other conditions as for Fig. 2.

TABLE IV

DETERMINATION OF GOLD IN CIP LEACH SOLUTIONS USING LIQUID CHROMATO-
GRAPHY AND ICPAES

The results are given in ppm.

Sample	CN column	C_{18} column	ICPAES
1	1.36	1.40	1.40
2	3.64	3.68	3.60

range 10 ppb* to 10 ppm. The leach solution typically consists of a mixture of cyano complexes in excess cyanide.

An important factor in assessing the suitability of liquid chromatography for use as an analytical method in the CIP process is the separation achieved between the base metals and the precious metals. With both of the columns used in the study described above, the silver(I)–cyano complex eluted early in the chromatogram and was therefore prone to interference from cyano complexes of base metals. The remaining precious metals eluted late in the chromatograms, however coelution of the cyano complexes of chromium(III) and platinum(II) on the C_{18} column was a drawback to the use of this column. The cyano column appeared to be well suited to the analysis because the precious metal–cyano complexes [except for silver(I)] appeared as a late eluting group, free from interference from the base metal complexes.

Fig. 4a shows a chromatogram obtained with the C_{18} column for the injection of a leach solution taken from a working CIP plant. The gold peak is clearly resolved and quantitation of silver is also possible. Fig. 4b illustrates the same sample separated on the cyano column. The gold content of two leach solutions was determined with both columns using the standard addition method. The results are given in Table IV, together with those obtained for the same samples using ICPAES. Excellent agreement between the chromatographic and spectroscopic methods was obtained.

Detection limits for silver, gold, platinum and palladium attainable with the chromatographic procedure are 1.9, 2.6, 0.9 and 0.8 ng, respectively. Precision data accumulated for ten replicate injections of 0.1 μg of gold [as the dicyanoaurate(I) complex] showed a relative standard deviation of 1.00% for peak area measurements and the calibration plot for gold was found to be linear at least up to 0.3 μg.

CONCLUSIONS

The chromatographic method developed for the separation of metal–cyano complexes has particular application to the analysis of gold processing leach solutions. Precious metals may be reliably determined and the method also provides additional geochemical information on the base metals present in the ore. When this information is required, the C_{18} column provides optimum performance in that up to eight cyano complexes may be resolved. Alternatively, the cyano column provides faster analysis because the superior resolution between complexes of precious and

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* Throughout this article the American billion (10^9) is meant.

base metals allows the mobile phase conditions to be altered to permit rapid elution of the precious metal complexes.

A major advantage of the chromatographic method over AAS and ICPAES is its ability to monitor one specific gold species. This factor is of particular importance to the CIP process since the success of the adsorption and subsequent stripping steps relies on the gold being present only as dicyanoaurate(I). The chromatographic procedure gives comparable results to those obtained by flame AAS, but avoids the time-consuming sample acidification and extraction steps required for AAS. In its present form, the developed method is not applicable to the analysis of CIP discharge solutions since these contain gold levels of less than 10 ppb. Studies are currently being directed towards a preconcentration system suitable for this analysis.

NOTE ADDED IN PROOF

Under alkaline conditions, low concentrations of ferrocyanide are readily converted to $[Fe(OH)(CN)_5]^{4-}$. It is therefore probable that this species is the form in which iron(II) is chromatographed.

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