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ION-INTERACTION REVERSED-PHASE CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF GOLD(I) CYANIDE IN MINE PROCESS LIQUORS USING AUTOMATED SAMPLE PRECONCENTRATION

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SUMMARY

Ion-interaction reversed-phase liquid chromatography is applied to the analysis of aurocyanide in liquors drawn from the carbon-in pulp (CIP) cyanidation process for the extraction and recovery of gold from its ores. Cyanide leach solutions containing low parts-per-million levels of gold may be directly analysed using a C_{18} column with acetonitrile–water (23:77, v/v) containing tetrabutylammonium ions as the eluent. Tailings solutions containing parts-per-billion levels of gold require sample preconcentration and this may be achieved using a C_{18} precolumn modified with the above ion-interaction reagent. An automated preconcentration system is described which permits matrix elimination on the concentrator column and use of a step-gradient to shorten the analysis time. The sample is loaded onto a precolumn equilibrated with acetonitrile–water (20:80, v/v) containing 5 m*M* tetrabutylammonium ions, and interfering cyano compexes are then selectively removed from the precolumn, after which the gold is eluted through an analytical C_{18} column using acetonitrile–water (30:70, v/v) containing the same ion-interaction reagent. Analysis of a CIP tailings solution taken from a working gold mine is illustrated.

INTRODUCTION

Analytical methodology for the determination of gold has been dominated by spectroscopic and electrochemical techniques, particularly atomic absorption spectroscopy (AAS). With AAS, the flame technique is applicable to parts-per-million concentration levels of gold, whilst the carbon furnace approach is applicable to much lower concentrations. Even with the latter technique, it is common to employ solvent extraction preconcentration as a means of lowering the detection limits to levels applicable to the analysis of real samples[1].

In recent years, the cyanidation process for extraction of gold from its ores has increased in popularity because it is suitable to very low grade ore materials. In this process, the ore is agitated in the presence of oxygen and excess cyanide to solubilise the gold as the aurocyanide anion, according to the reaction[2]:

$$2Au + 4CN^- + O_2 + 2H_2O \rightarrow 2Au(CN)_2^- + 2OH^- + H_2O_2$$

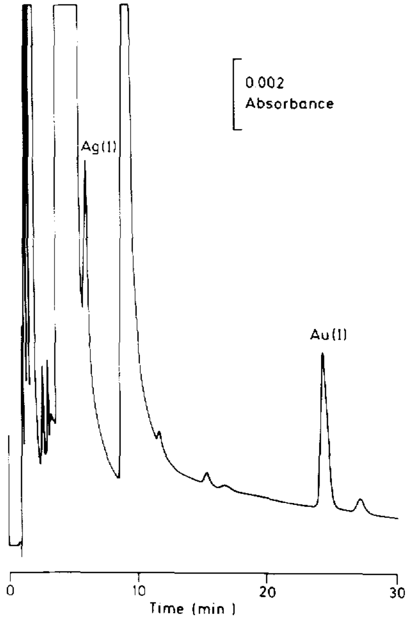


Fig. 1. Determination of aurocyanide in a cyanidation leach solution. Conditions: column, Waters Assoc. Nova Pak C_{18}, 150 × 3.9 mm I.D.; eluent, acetonitrile–water (23:77, v/v) containing 5 m*M* low UV PIC A; flow-rate, 1.0 ml/min; sample, 10 μl of the leach solution containing 1.4 ppm of gold. Reproduced from ref. 3.

The ore is reacted with 0.02–0.08% cyanide for up to 72 h, with lime being added to maintain an alkaline pH and to neutralise any acidic components of the ore. Under these conditions, other metals in the ore are also oxidised and are stabilised as their cyano complexes. The resulting gold leach solution is therefore contaminated with many other metal cyano complexes (at levels far in excess of gold) as well as excess cyanide. A listing of the typical composition of a leach solution has been reported[2].

In a previous paper[3], we have shown how ion-interaction reversed-phase liquid chromatography may be used for the determination of gold in a cyanidation leach solution containing gold at low parts-per-million levels. The chromatogram obtained for this analysis is shown in Fig. 1, and the analysis time may be decreased to less than 10 min, if the acetonitrile concentration in the eluent is increased to 30%. The chromatographic method has several advantages over alternative spectroscopic approaches. First, the method is specific for aurocyanide which is the most important form of gold for the subsequent recovery process; second, the sensitivity is excellent, with a detection limit of 40 ppb gold for an injection made using the stronger eluent mentioned above. Third, other metal cyanide complexes can be quantitated in the same run: important examples include platinum, palladium and silver, as well as some base metals.

Aurocyanide is recovered from the above leach solutions by adsorption onto activated carbon using the carbon-in-pulp (CIP) process. This process is favoured because it is easily automated and it more simple to control than alternative processes. Fig. 2 depicts a schematic representation of the CIP process. The cyanide

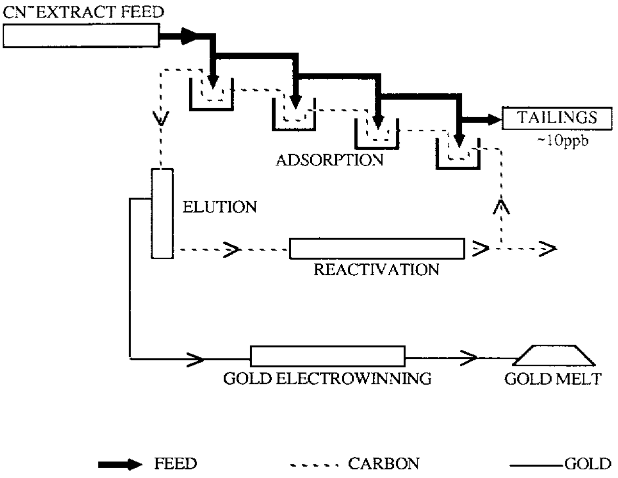


Fig. 2. Schematic flow diagram of the CIP process for the extraction and recovery of gold.

leach extract from the ore is fed in a countercurrent direction to tanks containing activated carbon and emerges as barren leachate containing very low levels of gold, typically of the order of 10 ppb. This barren leachate is then treated to become tailings. The loaded carbon is washed to remove most of the contaminant adsorbed metal cyano complexes and the aurocyanide is then stripped using relatively concentrated alkaline cyanide. Finally, the gold is recovered electrolytically and the carbon is reactivated and returned to the process.

The performance of the CIP process can be assessed by monitoring the gold levels present at various stages of the process. The concentration of gold in the process liquors may vary from the low ppm level (in the cyanide leachate) to low ppb levels (in the barren leachate and tailings). The most important indicator of the efficiency of the CIP process is obtained from the analysis of these latter solutions, and in this paper we report an automated preconcentration step-gradient method suitable for this purpose.

EXPERIMENTAL

Instrumentation

The liquid chromatograph consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model U6K injector, Model M590 programmable pump, Model 441 UV absorbance detector operated at 214 nm and an M730 data module. The preconcentration system initially comprised a single six-port high pressure switching valve, but was later modified to include two six-port pneumatically actuated valves and two low pressure pneumatically actuated solvent selection valves. All of these valves were conveniently combined in a single Waters automated valve switching (WAVS) unit which was operated electronically through the pump microprocessor and an appropriate events unit. The apparatus used is schematically illustrated in Fig. 3, and Fig. 4 shows details of the plumbing interconnections employed.

The analytical column was a Waters Assoc. Nova Pak C_{18} column (150 × 3.9

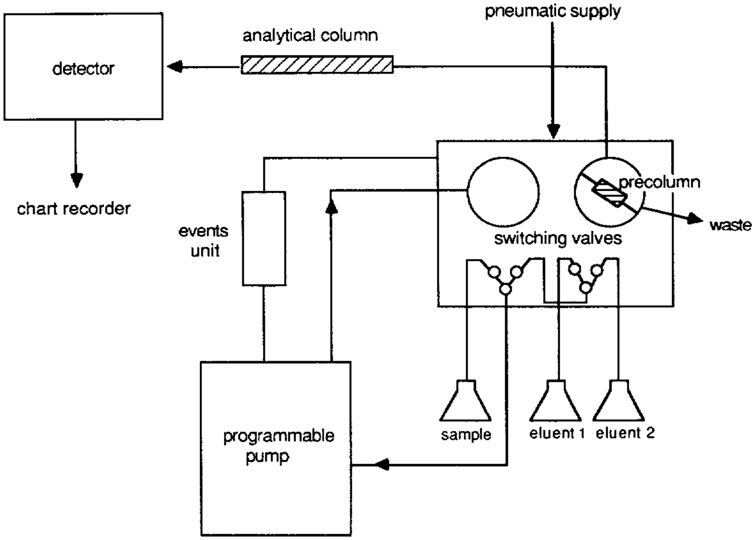


Fig. 3. Schematic diagram of the preconcentration system employed in this study.

mm I.D.) and the pre-column used for sample preconcentration was a Waters Assoc. C_{18} Guard-Pak (5.0 × 6.0 mm I.D.) housed in a Waters Assoc. Guard Pak Pre-column Module.

Reagents

The mobile phases used for ion-interaction separations comprised water treated with a Millipore (Bedford, MA, U.S.A.) Milli-Q water purification system, acetonitrile (Waters Assoc., chromatographic grade, UV cut-off 190 nm) and 5 m*M* low UV PIC A (Waters Assoc.) as the ion-interaction reagent. Mobile phases were prepared by diluting the appropriate amount of acetonitrile with water, adding the low

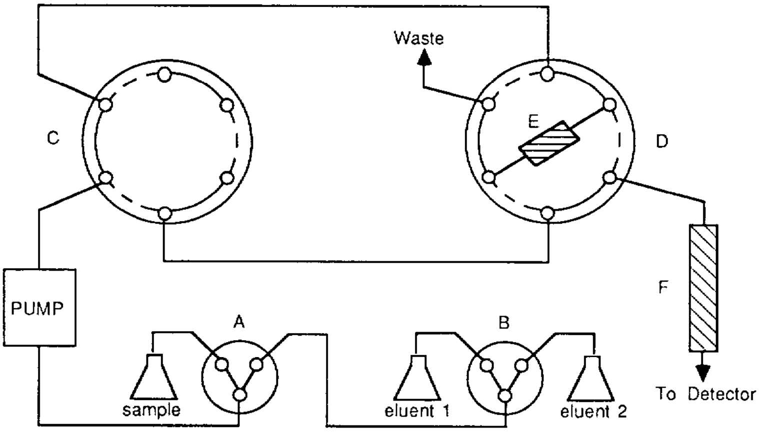


Fig. 4. Details of the valve interconnections used. A and B = low pressure solvent selection valves; C and D = six-port high pressure switching valves; E = C_{18} precolumn; F = analytical column.

UV PIC A to give a final concentration of 0.005 M, and then diluting to 1 l in a volumetric flask. The resulting solution was filtered through a 0.45-μm membrane filter and degassed in an ultrasonic bath before use. Eluent 1 consisted of acetonitrile–water (20:80, v/v) containing 5 mM low UV PIC A, whilst eluent 2 consisted of acetonitrile–water (30:70, v/v) containing 5 mM low UV PIC A.

A stock solution of aurocyanide was prepared by dissolution of an accurately weighed amount of the analytical grade potassium salt (Fluka AG, Switzerland) in 1000 ppm potassium cyanide solution made alkaline with sodium hydroxide. This solution was diluted as required in 100 ppm potassium cyanide solution to give the trace level standard solutions.

Throughout this paper, the concentrations of standard solutions (expressed as ppm or ppb) refer to the concentrations of metal present, rather than to concentrations of cyano complexes.

Chromatographic procedures

All chromatographic separations were carried out at room temperature using a mobile phase flow-rate of 1.0 ml/min, and the sample solutions were loaded onto the concentrator column at the same flow-rate.

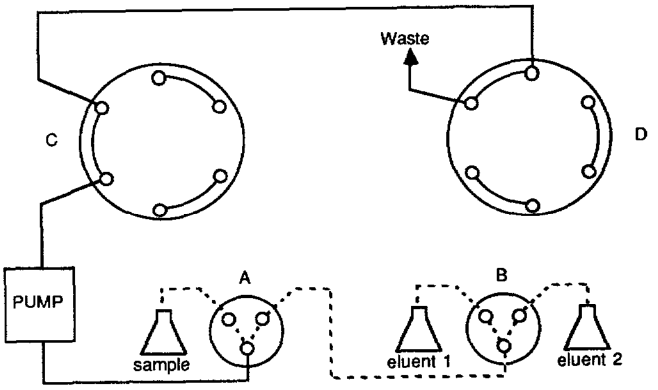
Preconcentration of samples was carried out by varying the flow-paths, using a similar sequence to that reported previously for preconcentrating trace levels of inorganic anions on fixed-site anion-exchange concentrator columns[4]. This sequence was adapted to include two eluents and step-gradient elution of the solutes, and details are shown in Fig. 5. The following steps were employed.

(a) Flushing the interconnecting tubing. Since only a single pump was to be used to deliver the sample and two different eluents, it was necessary to flush the interconnecting tubing with each solution prior to insertion of the analytical or concentrator column into the flow-path. The flushing step illustrated in Fig. 5 shows the manner in which this was achieved. The high pressure valves (C and D) were set to the configuration shown and the required solution was selected using appropriate settings of the low-pressure valves A and B. When the desired flow-path was configured, the solution was pumped through the tubing at high flow-rate (5 ml/min). In the sequence described below, the interconnecting tubing would be flushed whenever the composition of the pumped solution was altered; for example, flushing with sample would occur in preparation for step (b) below.

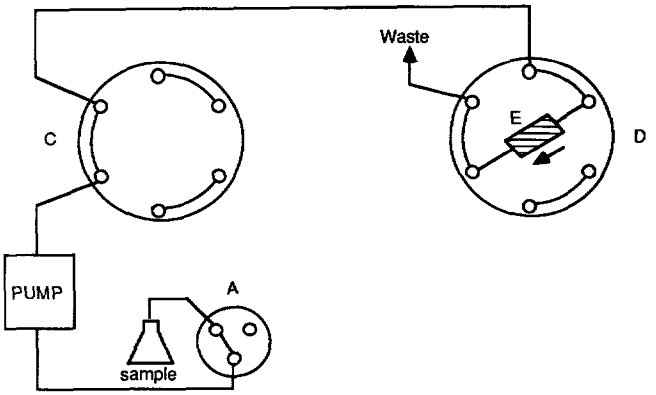
(b) Loading sample onto the concentrator column. The sample solution was selected with valve A and the concentrator column (E) was inserted into the flow-path by rotation of valve D. A measured volume of sample was then passed at an accurate flow-rate through the concentrator column in the flow direction shown in Fig. 5.

(c) Concentrator column washing. After flushing the tubing with eluent 1, the valves were set to the wash position and a small, accurately known volume of eluent 1 was pumped through the concentrator column in the same flow direction as that used for sample loading.

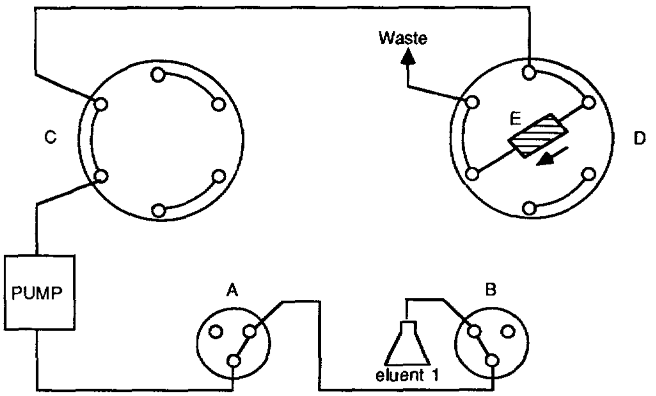
(d) Sample stripping. In this step, a small accurately known volume of eluent 1 was pumped through the concentrator column in the flow direction opposite to that in which the sample was loaded. This served to transfer the aurocyanide from the concentrator column to the analytical column (F).



FLUSH



LOAD



WASH

Fig. 5.

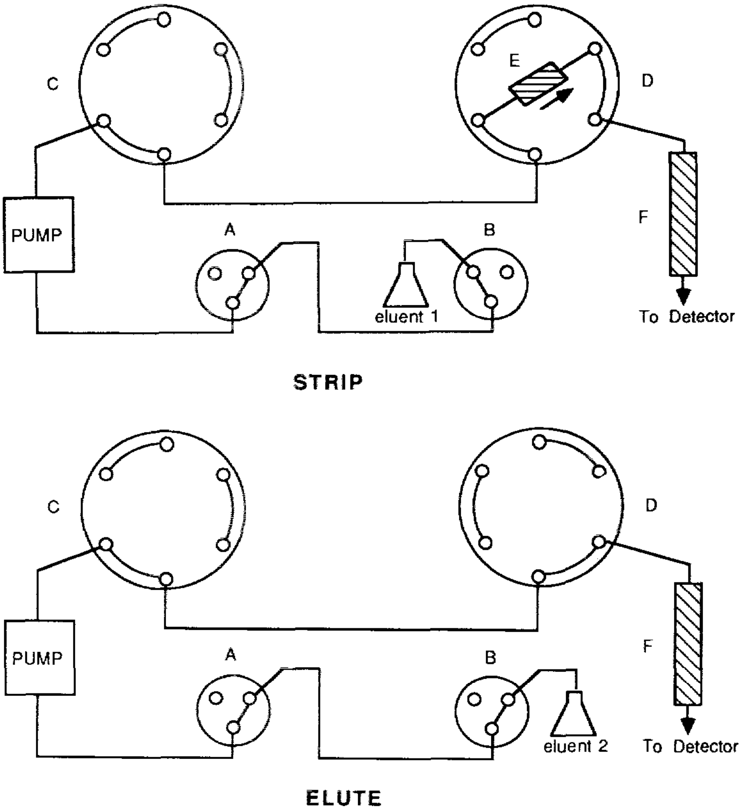


Fig. 5. Flow diagrams for the various steps in the preconcentration process (see text for discussion).

(e) Sample elution. After flushing the interconnecting tubing with eluent 2, the valves were rotated to remove the concentrator column from the flow-path and the aurocyanide eluted through the analytical column and detected in the usual manner.

Table I shows the duration and flow-rate of each of the above steps in a typical preconcentration run.

RESULTS AND DISCUSSION

Preconcentration using a single high-pressure valve

In a recent paper[5] we have reported a procedure for the preconcentration of ppb levels of aurocyanide in the presence of high levels (100 ppm) of cyanide, using a simple single high-pressure switching valve preconcentration system. This study showed that strongly bound species such as aurocyanide could be quantitatively retained on concentrator columns containing a reversed-phase material conditioned with a moderately hydrophobic ion-interaction reagent (in this case, tetrabutylammonium ions). The reversed-phase material is temporarily converted into an anion-exchanger and this characteristic persists during the preconcentration of sample

TABLE I

BASIC PROGRAM FOR THE PRECONCENTRATION AND ANALYSIS OF A TAILINGS SOLUTION

Eluent 1 = acetonitrile–water (20:80, v/v) containing 5 m*M* low UV PIC A. Eluent 2 = acetonitrile–water (30:70, v/v) containing 5 m*M* low UV PIC A.

Step	*Mode (see Fig. 5)*	*Solution delivered*	*Flow-rate (ml/min)*	*Volume (ml)*	*Function*
1	Wash	Eluent 1	1.0	10.0	Coat the surface of the precolumn with ion-interaction reagent
2	Flush	Sample	5.0	15.0	Flush tubing with sample
3	Load	Sample	1.0	2.0	Load sample onto precolumn
4	Flush	Eluent 1	5.0	15.0	Flush tubing with eluent 1
5	Wash	Eluent 1	0.4	0.8	Remove interfering cyano complexes from precolumn
6	Strip	Eluent 1	0.8	1.6	Transfer aurocyanide to analytical column
7	Flush	Eluent 2	5.0	15.0	Flush tubing with eluent 2
8	Elute	Eluent 2	1.0	15.0	Elute aurocyanide from analytical column

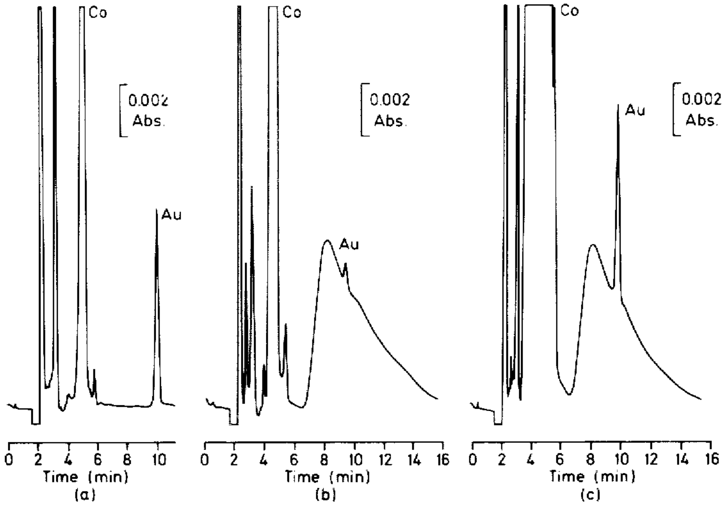


Fig. 6. Interference effect of hexacyanocobalt(III) on the determination of aurocyanide by preconcentration using a single-valve system. Conditions: analytical column, Waters Assoc. Nova Pak C_{18}, 150 × 3.9 mm I.D.; concentrator column, Waters Assoc. C_{18} Guard Pak, 5.0 × 6.0 mm I.D.; eluent, acetonitrile–water (30:70, v/v) containing 5 m*M* low UV PIC A; flow-rate, 1.0 ml/min. Samples: (a) 2 ml of 50 ppb aurocyanide and 50 ppb hexacyanocobalt(III) in 100 ppm cyanide; (b) 200 μl of 50 ppb aurocyanide and 5 ppm hexacyanocobalt(III) in 100 ppm cyanide; (c) 2 ml of 50 ppb aurocyanide and 5 ppm hexacyanocobalt(III) in 100 ppm cyanide. A single-valve preconcentration system was used, as described in ref. 5.

volumes up to 3 ml. Beyond this volume, non-quantitative binding of aurocyanide occurs, presumably due to loss of ion-exchange functionalities resulting from desorption of the bound ion-interaction reagent during loading of the sample. The detection limit attainable using an eluent comprising acetonitrile–water (32:68, v/v) containing 5 m*M* low UV PIC A was 0.43 ppb of gold, and it was shown that similar levels of palladium and platinum (as their cyano complexes) could be determined simultaneously.

This method was evaluated as a possible analytical approach for the determination of aurocyanide in CIP tailings solutions. Two potential effects of this matrix were envisaged. First, the binding of aurocyanide onto the concentrator column could be adversely influenced by the presence of excess concentrations of other metal cyano complexes in the sample. Second, co-elution of some of the matrix components with aurocyanide was possible.

To investigate these possibilities, elevated levels of a number of metal cyano complexes were added to a trace aurocyanide standard solution and the sample preconcentrated. This study showed that hexacyanocobalt(III) and hexacyanoiron(III) gave severe interference effects, whereas tetracyanonickel(II) interfered to a lesser extent. This interference appeared as a broad peak which coeluted with aurocyanide, as illustrated in Fig. 6 using hexacyanocobalt(III) as the interfering species. Several conclusions were evident from Fig. 6. In the first place, the interference occurred only when the cobalt was present at excess concentration (compare Fig. 6a and c). Second, the size of the aurocyanide peak was not diminished by the presence of excess cobalt (see Fig. 6a and c), however the coeluting interference would clearly detract from reliable quantitation of the aurocyanide peak. Finally, the size of the interfering peak was not proportional to the amount of cobalt in the sample (compare Fig. 6b and c). Further, when the column effluent corresponding to the interfering peak was collected and analysed for cobalt using inductively coupled plasma atomic emission spectrometry, no cobalt was detected. In view of this, it is possible that the interfering peak was a system peak resulting from disturbance of the multiple equilibria existing between the mobile and stationary phase components.

Numerous attempts were made to eliminate the co-eluting peak using hexacyanocobalt(III) as the interfering species since this complex was well retained on the concentrator column and produced the greatest interference of any species examined. Fig. 7 shows that reduction of the eluent strength to acetonitrile–water (20:80, v/v) enabled resolution of the aurocyanide from the interfering peak. Under these conditions, the aurocyanide appeared as a relatively broad, late eluting peak and the chromatogram was dominated by the large cobalt(III) peak. Improved chromatographic conditions were therefore sought.

Preconcentration using a multi-valve system

The previously employed preconcentration system was limited by its inability to accommodate on-column matrix elimination and step-gradient procedures. Both of these features were desirable in order to minimise the effect of high levels of metal cyano complexes and to decrease the analysis times. Thus a more complex preconcentration system was implemented, based on apparatus we have designed for the preconcentration of anions using fixed-site ion-exchange concentrator columns[4]. This system is described in detail in the experimental section (see Figs. 3–5) and provided a high degree of flexibility and control over the type and volume of eluent passed through the concentrator column, and the flow direction used.

On-column matrix elimination was achieved using the sample wash step shown

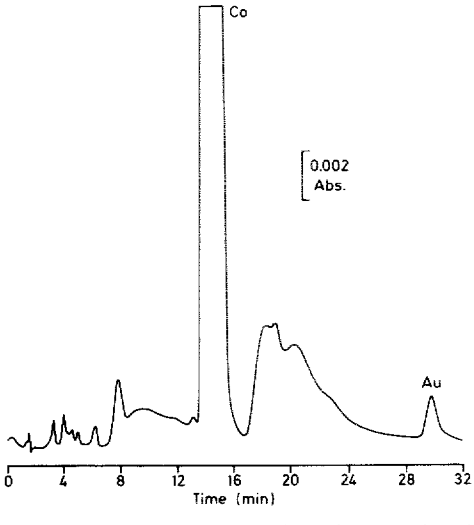


Fig. 7. Resolution of aurocyanide using a weaker eluent. Eluent, acetonitrile–water (20:80, v/v) containing 5 m*M* low UV PIC A. Sample: 2 ml of 50 ppb aurocyanide and 5 ppm hexacyanocobalt(III) in 100 ppm cyanide. Other conditions as for Fig. 6.

in Fig. 5. The rationale here was that the high degree of retention of aurocyanide on the concentrator column would permit removal of less strongly bound interferents by passage of a suitable volume of eluent through the column. In this way, the levels of interfering species transferred to the analytical column during the sample stripping step (see Fig. 5) would be reduced, thereby increasing the ruggedness of the analytical procedure. The utility of the wash and strip steps can be seen from Fig. 8, which shows the large peak obtained from a direct injection of 50 ppm of hexacyanocobalt(III) (Fig. 8a) and the much smaller peak obtained by preconcentration of twice as much solute but using the wash and strip steps (Fig. 8b). Neither of these steps has a deleterious effect on the preconcentration and analysis of aurocyanide (Fig. 8c).

It was expected that matrix elimination using the wash and strip steps would be most effective when carried out using the weak eluent employed in Fig. 7 since this eluent provided the greatest resolution between interfering species and aurocyanide. However, the quality of the final chromatogram would be enhanced if a stronger eluent was employed to elute the gold as a sharp peak in a reasonable time. For this reason, a step-gradient was invoked, wherein the percentage of acetonitrile in the eluent was increased from 20% for the sample loading, concentrator column washing and sample stripping steps, to 30% for the final analysis step.

This approach is applied to the preconcentration of aurocyanide in the presence of a 100-fold excess of hexacyanocobalt(III) in Fig. 9. Here, the wash and strip volumes have been optimised to produce the maximum matrix elimination during sample washing and to ensure quantitative transfer of gold during sample stripping.

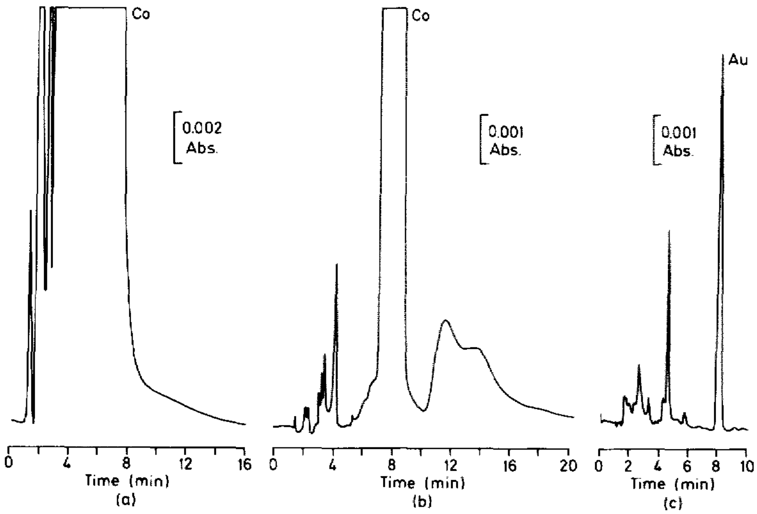


Fig. 8. Matrix elimination with the wash and strip steps using an automated preconcentration system. Conditions: wash volume, 200 μl; strip volume, 600 μl. Samples: (a) 100 μl direct injection of 50 ppm hexacyanocobalt(III) in 100 ppm cyanide; (b) preconcentration of 2 ml of 5 ppm hexacyanocobalt(III) in 100 ppm cyanide; (c) preconcentration of 2 ml of 50 ppb aurocyanide in 100 ppm cyanide. Other conditions as for Fig. 6, except that the preconcentration system shown in Fig. 3 was used. The wash and strip steps were not used in (a).

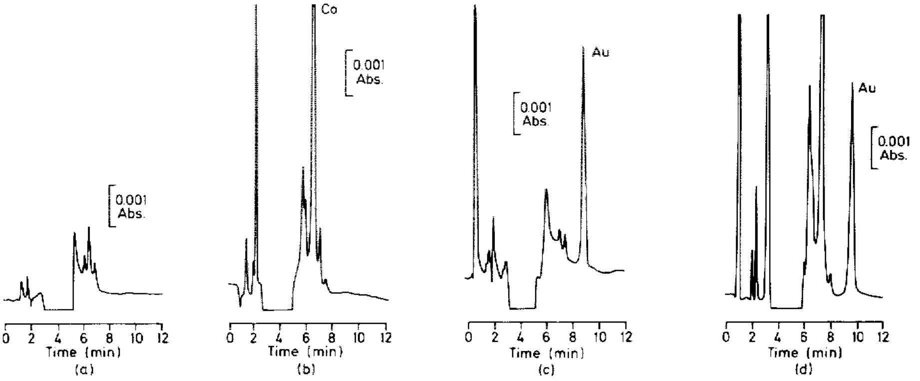


Fig. 9. Preconcentration with precolumn washing to achieve matrix elimination and using a step-gradient to shorten the analysis time. Conditions: eluent 1 (used for wash and strip steps), as for Fig. 7; eluent 2 (to shorten analysis time), as for Fig. 6; wash volume, 800 μl; strip volume, 1600 μl. Samples: (a) 2 ml of 100 ppm cyanide; (b) 2 ml of 5 ppm hexacyanocobalt(III) in 100 ppm cyanide; (c) 2 ml of 50 ppb aurocyanide in 100 ppm cyanide; (d) 2 ml 50 ppb aurocyanide and 5 ppm hexacyanocobalt(III) in 100 ppm cyanide. See Table I for details of the sequence used for sample preconcentration.

Fig. 9a shows a blank run obtained by preconcentrating 2 ml of 100 ppm cyanide solution. The negative baseline disturbance was the result of the changed eluent concentration produced by the step-gradient. Fig. 9b was obtained by preconcentrating a sample containing 5 ppm of hexacyanocobalt(III). The cobalt peak is very much reduced in comparison to those shown in Figs. 6 and 7, for which the same amount of cobalt was present in the sample. This illustrates the effectiveness of the sample washing step. Application of the same chromatographic conditions to the preconcentration of a 50 ppb aurocyanide sample gave the chromatogram shown in Fig. 9c. Standard addition experiments and comparison of the aurocyanide peak area to that obtained by direct injection of an identical amount of solute (*i.e.* 20 μl of 5 ppm aurocyanide) showed that the retention of aurocyanide on the concentrator column and its transfer to the analytical column were quantitative. The final chromatogram (Fig. 9d) illustrates the preconcentration of a sample containing 50 ppb aurocyanide and 5 ppm hexacyanocobalt(III). No interference was observed and the analysis time was reduced to less than 10 min. The same degree of success was obtained with similar levels of hexacyanoiron(III) and tetracyanonickel(II).

Application of the optimal chromatographic conditions to a CIP tailings solution obtained from a working gold mine is shown in Fig. 10. The composition of the tailings solution, as determined by inductively coupled plasma atomic emission spectrometry, is shown in Table II. It can be seen from Fig. 10 that the gold eluted as a well resolved, sharp peak which could be readily quantitated. Recovery experiments in which the sample was spiked with 10 ppb of aurocyanide gave an average recovery of 97.2% for triplicate determinations, which verified that the analysis was quantitative. The detection limit of this method is 0.43 ppb of gold[4].

It is clear that the nature of the tailings solution to be analysed will be entirely dependent on the type of ore which is being treated, and that wide variations in ore composition can be expected between different mining sites. For this reason, it must be anticipated that the analytical conditions developed in the present work will not

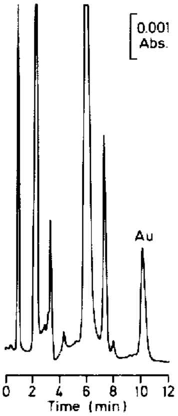


Fig. 10. Analysis of a CIP tailings solution from a working gold processing plant. The sample contained 25 ppb of gold. Conditions as for Fig. 9.

be applicable to all samples. However, the flexibility of the preconcentration system described enables the wash and strip volumes to be conveniently manipulated in order to accommodate wide variations in the sample matrix.

CONCLUSIONS

Ion-interaction reversed-phase liquid chromatography is a suitable technique for the determination of aurocyanide in CIP process liquors. Analysis of the cyanide leach solution can be achieved using direct injection of the sample because of the relatively high level (ppm) of aurocyanide present. Analysis of the more dilute tailings solutions requires a sample preconcentration method with matrix elimination on the concentrator column and use of a step-gradient to decrease the analysis time. These features have been incorporated into an automated preconcentration system, and this system can be readily adapted for differing sample matrices. It is highly feasible that an on-line instrument for gold analysis in CIP plants could be developed by

TABLE II

ELEMENTAL COMPOSITION OF THE TAILINGS SOLUTION ANALYSED IN FIG. 10

Element	*Concentration (ppm)*	*Element*	*Concentration (ppm)*
Al	0.4	Mg	1420
As	1.2	Mn	2.4
C	87 500	Na	15 700
Ca	480	Ni	1.0
Co	1.1	S	1050
Cu	12.1	Si	10.4
Fe	6.2	V	3.8
K	140	Zn	0.6

interfacing the analytical hardware described in this paper with a suitable device for acquisition of samples from process streams.

ACKNOWLEDGEMENT

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