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Determination of free cyanide in gold cyanidation process liquors by ion-interaction chromatography with post-column derivatization

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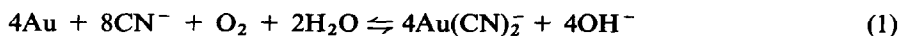
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ABSTRACT

A chromatographic method is described for the determination of high levels of free cyanide in leach liquors encountered in the cyanidation process for the dissolution of gold from its ores. The method also offers simultaneous determination of metallo-cyanide complexes and thiocyanate, which are also present in the sample. A 10- μ l aliquot of the sample is first separated by ion-interaction chromatography using a C₁₈ column, 25% (v/v) aqueous acetonitrile containing 5 mM low-UV PIC A as mobile phase, and UV detection at 214 nm. Cyano complexes of Cu(I), Fe(II), Ag(I), Fe(III) and Au(I) are detected, together with thiocyanate. Linear calibrations were obtained over the concentration ranges in which these species are found in leach liquors. The free cyanide in the sample is eluted at the column void volume and is detected by absorbance at 500 nm [together with thiocyanate and the copper(I) cyano complex] after post-column reaction with N-chlorosuccinimide, barbituric acid and isonicotinic acid to form a polymethine dye. The calibration plot for cyanide was linear over the range 0–300 ppm and no interferences from 1000 ppm levels of common anions were identified, except for sulfide which can be tolerated only up to 500 ppm. Alternative chromatographic hardware configurations offering heart-cut of the cyanide fraction and subsequent ion-exclusion separation of cyanide from other anions are discussed. When applied to leach liquor samples taken from operating gold mines, the chromatographic method is shown to give clean chromatograms and to offer superior accuracy and precision to the conventional silver nitrate titrimetric procedure, especially in the presence of high levels of copper in the sample. On-line operation of the method at a throughput rate of 3 samples per hour is also described.

INTRODUCTION

The most widely used process for extracting gold from its ores involves leaching of the ore with cyanide in the presence of oxygen. Under these conditions, metallic gold is solubilized as the aurocyanide ion, according to the equation [1]:



The aurocyanide is then recovered from the leach solution, usually by adsorption onto activated carbon. This process is known as carbon-in-pulp recovery and is favoured because of its simplicity and efficiency when applied to low-grade gold ores.

The rate of dissolution of gold depends on many factors, such as the free cyanide concentration, the oxygen level, the pH of the leach liquor, the concentration of other cyanide consuming species, and the physical characteristics of the ore. However, the single most important of these factors is the free cyanide concentration, which must be monitored at frequent intervals in order to maintain efficient gold dissolution. The optimal free cyanide concentration varies with the nature of the ore and the leaching conditions used, but is usually within the approximate range of 50–300 ppm.

In addition to the free cyanide and the solubilized gold, a typical leach liquor also contains numerous other species produced by reaction of cyanide with components of the ore. These species include other metal cyanide complexes (especially those of iron and copper) and thiocyanate. Determination of the free cyanide in such leach liquors may be approached using titrimetric methods, spectrophotometric methods, or by the use of ion-selective electrodes. Many titrimetric methods exist but the most common approach is to titrate the sample with standard silver nitrate to form $[\text{Ag}(\text{CN})_2]^-$, with a precipitate of $\text{Ag}[\text{Ag}(\text{CN})_2]$ being formed at the end-point [2]. Alternatively, the end-point can be detected with a silver sensitive indicator, such as potassium iodide or 5-(4'-dimethylaminobenzylidene)rhodanine [3]. Potentiometric end-point detection is sometimes applied when the sample solution is coloured. Abundant spectrophotometric methods for free cyanide are available in the literature and can be subdivided broadly into those based on the König reaction [4] and those involving metal complex formation {such as the formation of the $[\text{Ni}(\text{CN})_4]^{2-}$ complex [5]}. The König reaction, which converts cyanide to a polymethine dye, is the most widely used. Ion-selective electrodes of the solid-state [6] or membrane types [7] are also applicable to free cyanide determinations.

When applied to the routine monitoring of free cyanide in leach liquors, all of the above-mentioned analytical methods suffer from appreciable drawbacks. The spectrophotometric methods are prone to numerous interferences (such as sulfide and thiocyanate) which are likely to be present in the leach liquor, and do not have an appropriate linear calibration range for the concentration of cyanide typically encountered in such samples. The ion-selective electrode methods have the disadvantages of slow response, poor reproducibility and the requirement for sample dilution. The most rugged (and therefore the most frequently utilized) method is titration using rhodanine indicator, but this approach is very operator dependent, is not amenable to automation or on-line operation, and is also prone to interferences. Paramount amongst these interferences is the presence of copper cyanide complexes in the liquor. Copper(I) forms cyano complexes containing between 2 and 4 cyanide ions, with the most stable form being $[\text{Cu}(\text{CN})_2]^-$ ($\log K_f = 23.9$ [8]). Copper cyano complexes with 3 or 4 cyanide ligands are formed at high concentrations of cyanide and a significant amount of the cyanide bound in these complexes is titratable with silver nitrate. Thus, routine titration procedures applied to copper-containing ores can yield erroneously high results for free cyanide unless care is taken to account for the level of copper in the leach liquor. Failure to make this correction can lead to a decrease in the rate of gold dissolution in the leaching process and ultimately, a reduction in gold recovery.

For some years, we have been studying the chromatographic behaviour of metallo-cyanide complexes and we have shown that most of the stable complexes can be separated by ion-interaction chromatography and detected by UV absorbance at 214 nm [9]. Moreover, we have also demonstrated that the cyano complexes of gold

(I), platinum(II) and palladium(II) can be concentrated on a suitable pre-column and then separated by ion-interaction chromatography to give detection limits of less than 1 ppb ($\mu\text{g/l}$) [10]. This approach has been applied to the determination of gold in carbon-in-pulp tailings solutions [11]. In the present paper, these studies are extended to include the determination of high levels of free cyanide in carbon-in-pulp leach liquors, without interference from labile metallo-cyanide complexes or other ionic components of the leach liquor, including thiocyanate. Furthermore, this method also permits simultaneous determination of metallo-cyanide complexes in the leach liquor, so that information on both the free and bound forms of cyanide can be obtained from a single analysis.

EXPERIMENTAL

Instrumentation

Ion-interaction system. All liquid chromatographic instrumentation used in this work was manufactured by Waters Chromatography Division of Millipore (Milford, MA, USA). The basic hardware comprised an ion-interaction chromatographic system, which was used to separate free cyanide from other constituents of leach liquor. This system consisted of a Model 510 pump, Model U6K injector, Model 441 fixed-wavelength absorbance detector operated at 214 nm, and a Model Baseline 810 data station. A Nova-Pak C_{18} column (150×4.6 mm I.D.) was used.

Post-column reaction system. The post-column reaction system for derivatization of free cyanide consisted of a Waters dual-pump post-column pumping system and two knitted open tubular reaction coils containing 40 cm and 30 m, respectively, of 0.22 mm I.D. PTFE tubing. Further details of this system are given later. The derivatized free cyanide was then passed to a Model 484 variable-wavelength absorbance detector operated at 500 nm. The output of this detector was recorded by the data station.

Hardware configurations. The basic ion-interaction system and the post-column reaction system were interfaced in several ways, as shown in Fig. 1. In the simplest case, shown in Fig. 1a, the effluent emerging from the UV detector in the ion-interaction system was passed directly into the post-column reactor (PCR). This approach will be referred to as a "tandem" system. The second approach (Fig. 1b) involved passing the effluent from the UV detector in the ion-interaction system through a 6-port rotary valve. This valve could direct the effluent either to waste or to the post-column reactor. In this way, a selected portion (or "cut") of the effluent could be transferred to the post-column reactor. A second Model-510 pump was employed to carry the sample to the post-column reactor. Rotation of the 6-port valve was accomplished by pneumatic pressure, under the control of the computer data station. This method will be referred to as a "cut" system. The third configuration (Fig. 1c) was identical to the "cut" system, except that a Millipore Waters Fast Fruit Juice ion-exclusion column (150×7.8 mm I.D.) was inserted prior to the post-column reactor as a means of separating free cyanide from any components co-eluted from the ion-interaction system. This approach will be referred to as a "coupled" system.

On-line system. On-line operation was employed in the latter stages of this work. This was accomplished by use of a Filtrate Master (Flow Measurement Services, Perth, Australia) filtration unit, which was inserted into a 500-l tank of carbon-

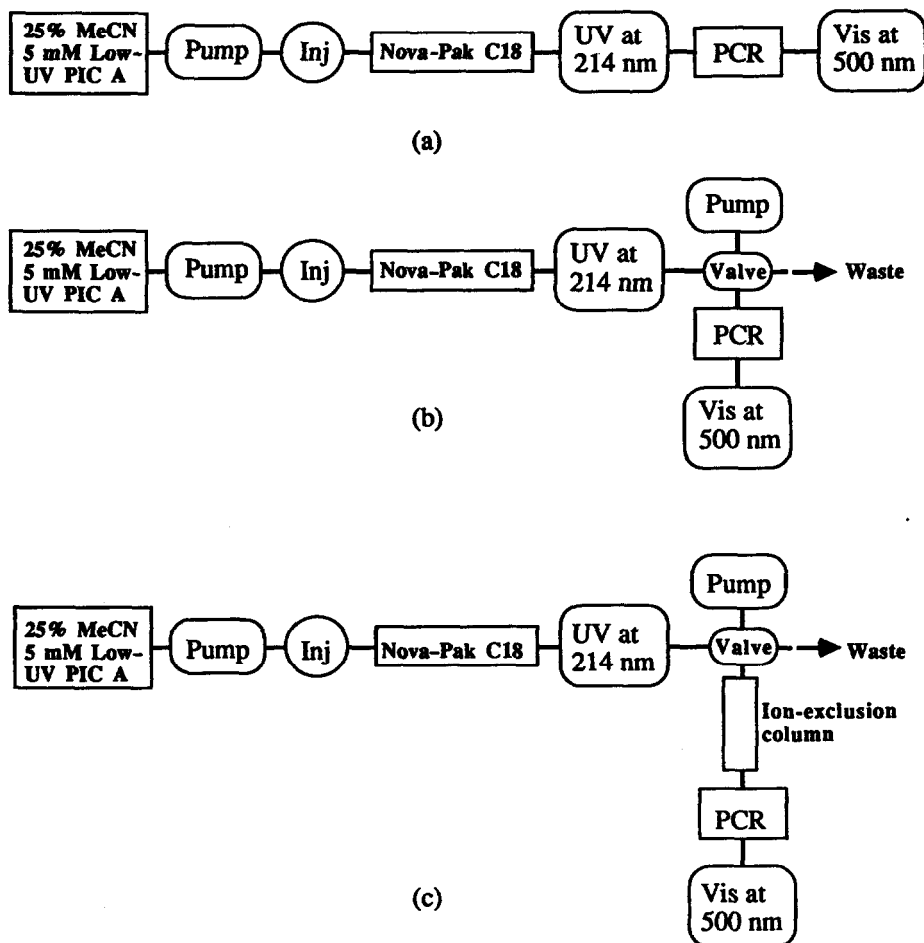


Fig. 1. Chromatographic hardware configurations used in this study. The post-column reactor is designated by PCR. (a) "Tandem" system, (b) "cut" system, (c) "coupled" system (MeCN = acetonitrile).

in-pulp leach liquor taken from an operating gold mine. The leach liquor was agitated using an electric motor connected to a suitable impeller. The filtrate from the Filtrate Master unit was pumped to a 10- μ l sample loop connected across a 6-port high pressure rotary valve. This valve replaced the injector in the ion-interaction system. The position of the valve was controlled by the computer data station and rotation of the valve was achieved with pneumatic pressure. Filtered leach liquor was passed continuously through the 10- μ l sample loop and the contents of the loop were injected into the chromatographic system, as required, by use of the appropriate valve position.

Reagents and procedures

All reagents used were of analytical-reagent grade. N-Chlorosuccinimide, succinimide, barbituric acid and isonicotinic acid were obtained from Aldrich (Mil-

waukee, WI, USA). Potassium aurocyanide was purchased from Johnson and Matthey Chemicals (London, UK), whilst potassium salts of the cyano complexes of Ag(I), Cu(I), Fe(II) and Fe(III) were synthesized according to published methods [12]. Chromatographic grade acetonitrile (UV cut-off 190 nm) was obtained from Millipore Waters. The mobile phase used in the ion-interaction chromatographic system comprised a 25% (v/v) aqueous solution of acetonitrile in 5 mM low UV PIC A, which was obtained from Millipore Waters. The carrier fluid used in the "cut" system shown in Fig. 1b was acetonitrile-water (25:75, v/v), and water served as the eluent for the ion-exclusion column used in the coupled system shown in Fig. 1c. All eluents were filtered through a 0.45- μ m membrane filter and degassed in an ultrasonic bath prior to use. The flow-rate was 1 ml/min in all cases.

Two reagents were used in the post-column reactor, as shown in Fig. 2. The first reagent consisted of 0.1% (w/v) N-chlorosuccinimide and 1% (w/v) succinimide. A stock solution of 10% succinimide in water was prepared and the post-column reagent was prepared by dissolving 0.1 g of N-chlorosuccinimide in 10 ml of the succinimide stock solution, followed by dilution to 100 ml with water, in a volumetric flask. The reagent was prepared daily. The second post-column reagent consisted of 0.5% (w/v) isonicotinic acid and 0.25% (w/v) barbituric acid dissolved in dilute lithium hydroxide solution, after which the solution was buffered to pH 7.0 with phosphoric acid. Addition of the buffer was essential to maintain stability, and under the conditions described, the reagent was stable for 3 weeks. Both of the post-column reagents were filtered through a 0.45- μ m membrane filter before use. The flow-rate of the N-chlorosuccinimide-succinimide reagent was 0.4 ml/min, and the same flow-rate was used for the isonicotinic acid-barbituric acid reagent. Further details on the post-column reactor are shown in Fig. 2.

RESULTS AND DISCUSSION

Selection of analytical methodology

The first step in the development of a chromatographic procedure for the determination of free cyanide in carbon-in-pulp leach liquors was to identify chromatographic conditions under which free cyanide could be separated from as many of the components of the leach liquor as possible. Coupled with this requirement was the desire to resolve those key components of the leach liquor which might yield important analytical information to the plant operator. We identified these key components as thiocyanate and the cyano complexes of silver(I), copper(I), iron(II), iron(III) and gold(I). From our previous experience with the separation of these complexes, and

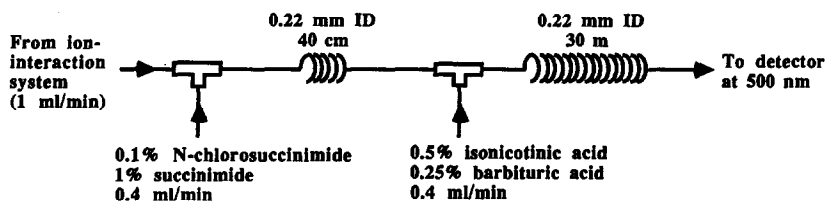


Fig. 2. Details of the post-column reactor used.

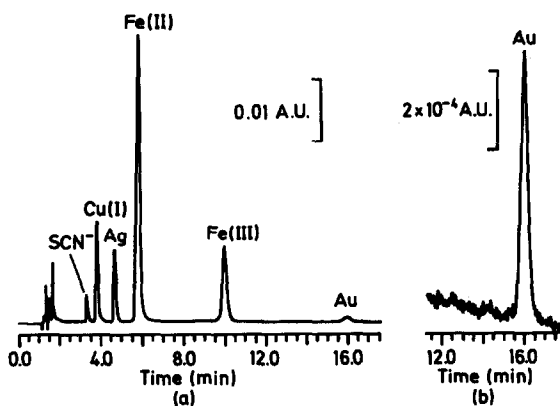


Fig. 3. Chromatogram obtained for the separation of free cyanide, thiocyanate and some metallo-cyano complexes by ion-interaction chromatography. Note that the free cyanide is not detected. Conditions: Waters Nova-Pak C₁₈ column, with 25% (v/v) aqueous acetonitrile containing 5 mM low-UV PIC A as eluent at a flow-rate of 1 ml/min, with detection by UV absorbance at 214 nm. A 10- μ l injection volume was used. Solute concentrations: SCN⁻ (3 ppm), cyano complexes of Cu(I) (1.5 ppm), Ag(I) (2 ppm), Fe(II) (2 ppm), Fe(III) (2 ppm) and Au(I) (1 ppm); CN⁻ (100 ppm). A higher scale expansion was used for (b) than for (a).

with the aid of a computer-assisted technique for selection of the optimal mobile phase composition, we found that 25% (w/v) acetonitrile in 5 mM low-UV PIC A was a suitable mobile phase. The separation achieved using this mobile phase with a Nova-Pak C₁₈ column is shown in Fig. 3a. In this chromatogram, the concentrations of the species approximate those likely to be present in a carbon-in-pulp leach liquor. It can be seen that all components are well resolved and that the gold(I) peak can be quantified readily by appropriate scale expansion on the data system (Fig. 3b). Calibration plots constructed for all the species shown in Fig. 3 were linear up to the maximum concentrations tested, which were as follows: 300 ppm for thiocyanate and copper(I), 50 ppm for iron(II) and 20 ppm for iron(III), silver(I) and gold(I). It should be noted that these concentrations refer to the metal ions rather than to the complexes themselves.

The free cyanide eluted from the column is not detected at 214 nm, but collection and derivatization of mobile phase fractions revealed that this species was unretained on the column and was eluted at the void volume. It was therefore feasible that the small volume of mobile phase containing the free cyanide could be further analyzed to determine the free cyanide concentration. To accomplish this, it was necessary to select appropriate analytical methodology to permit the determination of the eluted free cyanide in the presence of the mobile phase components and of any co-eluted components of the leach liquor. Moreover, any analytical technique used should be amenable to on-line operation so that the analysis could be automated. After consideration of these constraints, several possibilities existed, including the use of ion chromatography with conductometric or amperometric detection, and spectrophotometry using a flow-through reactor. We investigated the use of ion chromatography using anion-exchange columns, but this approach was abandoned because of interferences caused by acetonitrile and tetrabutylammonium ions (from the low-UV

PIC A). In addition, it was found that common inorganic anions present in the leach liquor, such as chloride and sulphate, were co-eluted with free cyanide on the ion-interaction system and these either eluted from the ion-exchange column at the same time as cyanide or were so strongly retained that excessive run times were necessary. On the other hand, a selective spectrophotometric reaction appeared more suitable, provided that any interfering species present in the free cyanide band could be removed. For this reason, we examined a wide range of spectrophotometric procedures for cyanide which could be adapted to a continuous flow system.

Chemistry of the post-column reaction

Many derivatisation reactions have been developed for the analysis of cyanide, with the single most common method involving variations of the König reaction [4]. These reactions were chosen for investigation in view of their high selectivity towards cyanide and because they have been utilized in continuous-flow, flow-injection and post-column reaction analysis systems [13,14].

The König reaction can be considered as three separate steps: (i) Chlorination (or bromination) of cyanide to give cyanogen chloride, a source of CN^+ . (ii) Reaction of the CN^+ with pyridine or a pyridine derivative to produce a conjugated dialdehyde intermediate. (iii) Coupling of this aldehyde with one or two molecules of an aromatic amine or a compound containing reactive methylene protons to produce a conjugated, resonance stabilised polymethine dye [15,16].

Chlorination is preferred in a closed post-column reaction system since bromination requires the addition of arsenite to destroy the excess bromine which would otherwise prevent the formation of the dye [17]. The usual chlorination reagent is chloramine-T, but this reagent is not optimal for use in flow-through reactors because of the likelihood of precipitate formation. An alternative chlorination reagent, N-chlorosuccinimide [15], was found to be more suitable because its reaction product, succinimide, was soluble in water.

Pyridine and two of its derivatives, 4-methylpyridine (4-picoline) [18] and pyridine-4-carboxylic acid (isonicotinic acid) [19,20], have been used to form the dialdehyde. Pyridine has been used widely, but in view of the toxicity and unpleasant odours of pyridine and 4-picoline, we preferred to use isonicotinic acid, which is odourless and has minimal toxicity.

The most commonly used coupling reagent at present is barbituric acid [21], whilst others have included 3-methyl-1-phenyl-2-pyrazolin-5-one (pyrazolone) [22], *p*-phenylenediamine [23], benzidine [17], anthranilic acid [24], sulphanilic acid [25] and amsonic acid [26]. Benzidine is a carcinogen and *p*-phenylenediamine is a suspected carcinogen [27]. We have elected to use barbituric acid on the basis of toxicity considerations and ease of reagent preparation.

The reaction scheme for the derivatization of cyanide is shown in Fig. 4. N-Chlorosuccinimide (I) reacts with cyanide to produce cyanogen chloride and succinimide (II). The cyanogen chloride further reacts with isonicotinic acid (III) to give the intermediate product (IV) which hydrolyses to the dialdehyde (V). Barbituric acid (VI) condenses with the dialdehyde to produce a dye species (VII), which on standing condenses with a further molecule of barbituric acid to give a second polymethine dye (VIII). Several authors have noted that there are two distinct wavelengths of maximum absorbance associated with this reaction [19,20]. The first absorbance maximum

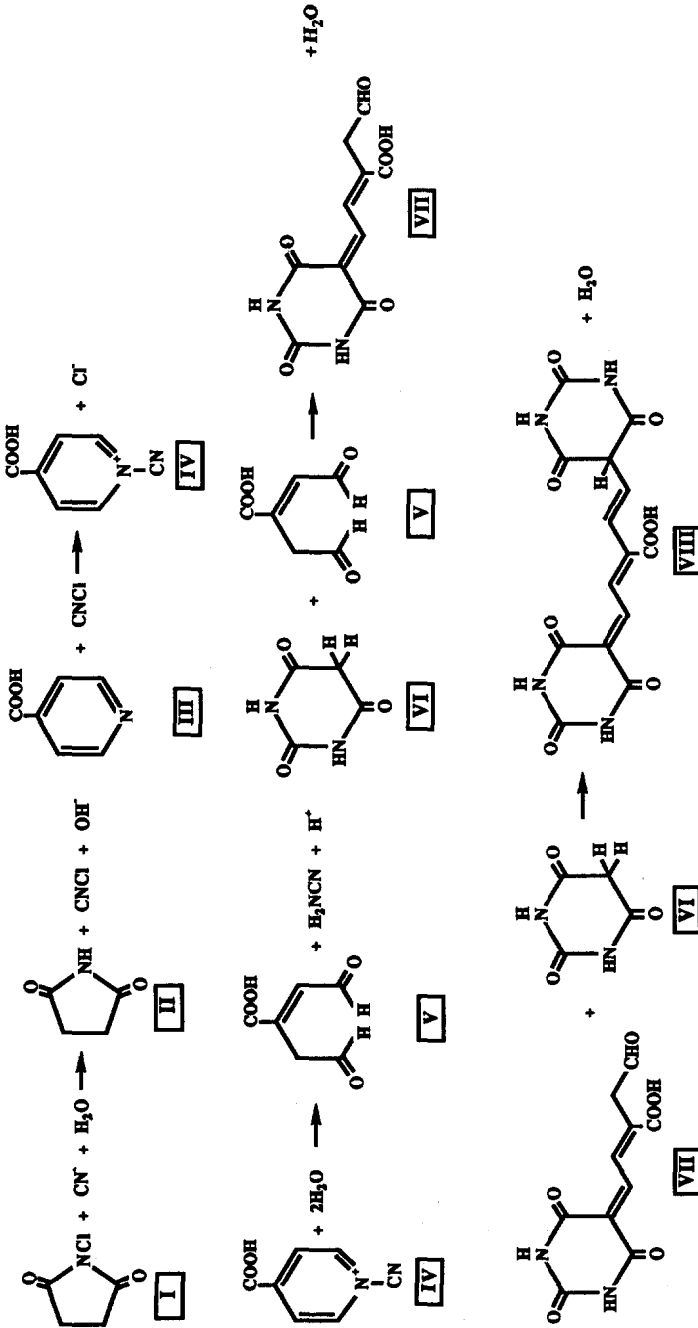


Fig. 4. Reaction scheme for the post-column derivatization. See text for discussion. I = N-Chlorosuccinimide; II = succinimide; III = isonicotinic acid; IV = reaction intermediate; V = pent-2-enial-3-carboxylic acid; VI = barbituric acid; VII = first dye species; VIII = second dye species.

appears rapidly at 525 nm and is due to the formation of the first dye species (VII). The second maximum occurs at 600 nm and is attained after approximately 15 min. This maximum is due to the formation of the polymethine dye (VIII) and is of greater magnitude than the first absorbance maximum. Under flow-through reaction conditions, the first maximum is the most useful because of its rapid formation and was therefore applied in this work.

The reaction conditions were then optimized to provide a suitable response to the range of cyanide concentrations expected in the samples to be analyzed. The detection wavelength was altered to 500 nm to reduce sensitivity and the isonicotinic acid and barbituric acid concentrations were varied until linearity of the cyanide calibration plots was achieved. The method was further modified by buffering the isonicotinic acid–barbituric acid reagent to pH 7.0 with phosphoric acid. This avoided the requirement to add a phosphate buffer as a post-column reagent (as used by Toida *et al.* [14]), improved the stability of this reagent, and provided a suitable pH for dye formation.

It was found that a gradual decrease in the absorbance of a derivatized 100 ppm cyanide standard in 10 mM lithium hydroxide was observed. This was attributed to instability of the N-chlorosuccinimide–succinimide reagent and could be prevented if this reagent was prepared freshly on a daily basis.

Evaluation of hardware configurations

As can be seen from Fig. 1, there are three possible ways in which the post-column reactor can be coupled to the ion-interaction chromatographic system. The “tandem” approach is the simplest, but has the disadvantage that all components of the leach liquor, including those which are co-eluted with free cyanide, are passed to the reactor. The use of a switching valve to select a desired portion of the free cyanide band (*i.e.*, the “cut” system shown in Fig. 1b) partly obviates this disadvantage but introduces the further problem of deciding which portion of the cyanide band should be passed to the post-column reactor. Full separation of the free cyanide from any co-eluted species can be achieved by passing the cut fraction through a suitable chromatographic column (*i.e.*, the “coupled” system shown in Fig. 1c), but again, the timing of the cut is critical. Preliminary experiments showed that free cyanide could be resolved from most common inorganic anions and all metallo–cyanide complexes which are weakly retained on the ion-interaction system by use of an ion-exclusion column with water as eluent. Under these conditions, the cyanide is present predominantly as undissociated hydrocyanic acid, which is moderately well retained on the ion-exclusion column used (Millipore Waters Fast Fruit Juice column). In contrast, all fully ionized inorganic species are unretained.

Chromatograms from injections of cyanide were obtained for each of the possible hardware configurations. Well-shaped peaks for the derivatized cyanide were observed in all cases. When the “coupled” system was employed, with water as eluent for the ion-exclusion column, cyanide was eluted at a retention time of 6.9 min. In comparison, fully ionized inorganic anions were eluted at the column void time (2.2 min), showing that these species were well resolved from the peak for free cyanide.

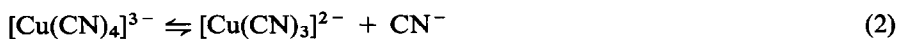
Calibration plots were constructed for each hardware configuration over the range 0–300 ppm of free cyanide, using 10- μ l injections onto the ion-interaction chromatographic system. All hardware configurations yielded linear calibrations. Precision was less than 1% relative standard deviation (R.S.D.) for each system.

These results suggest that all three hardware configurations could be applied successfully to the determination of free cyanide in leach liquors. Clearly, the mechanical complexity of the system increases as one moves from the "tandem" to the "coupled" systems, but at the same time, the ability of the system to tolerate interferences increases. The choice between the hardware configurations is therefore dependent on the types of interferences observed in the particular post-column reaction employed.

Interferences

Known interferences in the König reaction used in this study include thiocyanate, labile metallo-cyanide complexes and sulfide. The first two of these yield positive interference by producing coloured reaction products which absorb at the detection wavelength, whilst sulfide gives negative interference by reacting with the oxidant. Under the chromatographic conditions used in the ion-interaction system, free cyanide is separated from both thiocyanate and $[\text{Cu}(\text{CN})_4]^{3-}$, which is the only labile cyano complex likely to be present in appreciable concentrations in the samples analyzed. Common inorganic anions, including sulfide, are partially co-eluted with the free cyanide. The interference effects of these ions were examined by preparing 100-ppm cyanide standards containing 1000 ppm of each potential interferent. The peak area for free cyanide was altered by less than 1% for chloride, sulfate, nitrate, nitrite and phosphate, whilst sulfide caused a moderate interference (20%) at this level. A more detailed study of the interferences effects of sulfide was undertaken and showed that this interference is not evident for sulfide concentrations up to 500 ppm. Sulfide interference can be overcome using the "coupled" chromatographic system, but this was not considered necessary for the samples analyzed because the sulfide levels were below the interference threshold. Moreover, sulfide may be removed easily before analysis by treatment of the sample with lead acetate, followed by filtration.

The question of interference effects from $[\text{Cu}(\text{CN})_4]^{3-}$ merits further examination. This species is likely to be present in samples which have significant copper content and also a high level of free cyanide (e.g. 50 ppm). Whilst the copper complex itself is separated from free cyanide, the dissociation equilibrium of this complex (see eqns. 2 and 3) will contribute some free cyanide to the solution:



The equilibrium constant for eqn. 2 is $3.16 \cdot 10^{-2}$, whilst that for eqn. 3 is $5.01 \cdot 10^{-6}$ [8]. Injection of $[\text{Cu}(\text{CN})_4]^{3-}$ should therefore produce a small peak for free cyanide, and this is observed in practice. When the level of free cyanide is high, as is the case for leach liquors, both of the above equilibria will be forced to the left. It would therefore be expected that a mixture of $[\text{Cu}(\text{CN})_4]^{3-}$ and free cyanide should produce two peaks after the post-column reaction, the first being due to free cyanide and the second resulting from dissociation of the labile copper cyano complex in the post-column reactor. Again, this corresponds to the observed behaviour. A series of experiments was performed in which increasing amounts of $[\text{Cu}(\text{CN})_4]^{3-}$ were added to solutions of 100 ppm and 500 ppm free cyanide and these solutions were injected. It

was found that the free cyanide peak height for the 100-ppm cyanide solution showed a small increase as the concentration of added copper was increased. Moreover, this increase was in approximate accordance with the calculated levels of free cyanide which would be produced from dissociation of the complex according to eqns. 2 and 3. However, there was virtually no change in the cyanide peak for the 500 ppm solutions, even when 300 ppm of $[\text{Cu}(\text{CN})_4]^{3-}$ was added. This effect was due to suppression of the dissociation of the complex as a result of the high level of free cyanide. The chromatographic system used in this work should therefore provide a true measure of the free cyanide present in the sample, without interference from copper cyano complexes.

These interference studies suggest that the simplest hardware configuration, namely the "tandem" system, should be applicable to the analysis of many leach liquor samples. This configuration was therefore applied to a series of real samples and these analyses are discussed below.

Applications to the analysis of leach liquors

The proposed method was applied to a number of leach liquors taken from operating carbon-in-pulp processing plants. Chromatograms were obtained by direct injection of 10 μl of the filtered leach liquor and a typical chromatogram is shown in Fig. 5. Considering the complexity of the sample, the chromatogram is remarkably clean and permits ready quantification of the metallo-cyanide complexes, as well as free cyanide and thiocyanate. It will be noted that the chromatogram recorded after the post-column derivatisation reaction (Fig. 5c) shows peak for thiocyanate and $[\text{Cu}(\text{CN})_4]^{3-}$, as well as for free cyanide. However, these components are well resolved from free cyanide and do not interfere.

A comparison of free cyanide values obtained by the proposed method and by titration with silver nitrate using the rhodanine indicator was undertaken. The results obtained for two particular samples are representative of this study and are shown in Table I. Sample A was low in copper (1.7 ppm) and there was very good agreement

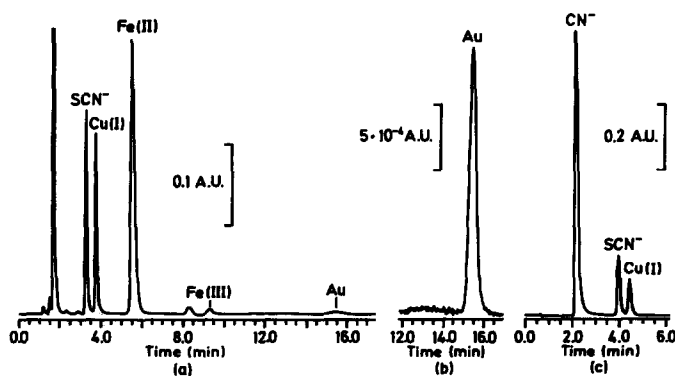


Fig. 5. Chromatogram obtained for a leach liquor. The sample injection volume was 10 μl . Chromatographic conditions as for Fig. 4; post-column reaction conditions as for Fig. 3. The "tandem" hardware configuration (Fig. 1a) was used. The output of the UV detector is shown in (a) and (b), whilst (c) shows absorbance at 500 nm after post-column reaction.

TABLE I

COMPARISON OF TITRIMETRIC AND CHROMATOGRAPHIC METHODS FOR THE DETERMINATION OF FREE CYANIDE IN LEACH LIQUORS

Sample	Copper content (ppm)	Free cyanide (ppm)			
		Titration method	Tandem system	Cut system	Coupled system
A	1.7	56.6	57.2	56.3	52.6
B	140	134	116	—	—

between the cyanide levels obtained by titration and those for the proposed method, using each of the hardware configurations. This agreement confirms the accuracy of the proposed method since the titrimetric method is known to be reliable when the level of copper is low. On the other hand, sample B contains 140 ppm of copper and it can be seen from Table I that the titrimetric method yielded a higher result for free cyanide than did the chromatographic method. This disparity can be attributed to interference of the copper cyano complex in the titrimetric procedure. Moreover, the precision of the titrimetric method for sample B was very poor (11% R.S.D.), whilst that for the chromatographic method was good (0.2% R.S.D.).

Limited experiments were carried out to show the feasibility of on-line operation of the chromatographic method. A filtration probe was inserted into the leach liquor and the filtrate emerging from this unit was found to be free of particulate material of diameter greater than 0.5 μm . This filtrate was therefore suitable for chromatographic analysis and was pumped directly to the sampling loop and thence to the liquid chromatograph. Analyses were performed at the rate of 3 samples per hour and excellent reproducibility was obtained for replicate chromatograms. These results suggest that the method can be adapted readily for on-line use, provided that the analytical hardware can be sited in relatively close proximity to the leach tank in order to prevent loss of cyanide transport of the sample to the instrument.

CONCLUSIONS

The proposed chromatographic method offers a simple approach to the simultaneous determination of free cyanide, metallo-cyanide complexes and thiocyanate in cyanidation leach liquor samples. No significant interferences were found with the derivatisation chemistry used in this work, but in the event that alternative post-column derivatisation reactions are preferred, it is possible to employ the coupled chromatographic system in order to further separate the free cyanide from potential interferences. Precision and accuracy of the chromatographic procedure are good and the method is amenable to on-line operation. A field trial of this system in a working gold processing plant is currently in progress.

ACKNOWLEDGEMENTS

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is gratefully acknowledged. Patent applications on the technology described in this paper are pending.

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