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Monitoring the cyanidation of gold–copper ores with ion-interaction chromatography
Determination of the CN^-:Cu(I) molar ratio

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Abstract

The use of reversed-phase ion-interaction high-performance liquid chromatography is reported for process monitoring of cyanide, thiocyanate and metallo–cyanide species in the gold cyanidation process. Thiocyanate and the metallo–cyanide complexes were monitored with a programmable, variable-wavelength UV detector mounted directly after the column, while cyanide, thiocyanate and the Cu(I) and Ag(I) cyanide complexes were monitored with a post-column reaction (PCR) detection system mounted after the UV detector. The eluent composition was optimised to enable separation of the major components of process samples in less than 10 min on a 5 cm column, but a 15 cm column was required for samples that contained Cu(I) at concentrations in excess of 300 ppm. The major emphasis during development of the eluent was to provide baseline resolution of thiocyanate and the Cu(I)–cyanide peaks and the optimal eluent composition consisted of 25% acetonitrile, 10 m*M* tetrabutylammonium hydroxide, 10 m*M* KH_2PO_4, 5 m*M* H_2SO_4 and 80–160 μ*M* NaCN, adjusted to pH 8.0. The level of cyanide present in the eluent was determined by the degree of separation required between thiocyanate and Cu(I). The PCR detection system enabled the cyanide:copper molar ratio, *R*, in process samples to be monitored routinely. *R* was determined from the peak area ratio of the cyanide and Cu(I)–cyanide peaks. The use of the peak ratio eliminated drift in the PCR detection system, providing a stable calibration for *R*. Good agreement was observed between standard analytical methods and the chromatographic method for determining *R*. Controlled cyanide leach tests showed that all the cyanide in the samples could be accounted for by the various cyano species detected. The proposed method has been utilised under field conditions on a working gold mine and has been shown to be very useful for determining cyanide losses and for monitoring the gold leaching process when treating cupriferous and pyritic gold ores.

Keywords: Process monitoring; Cyanide; Thiocyanates; Metallo–cyanide complexes; Inorganic anions; Copper–cyanide complexes

1. Introduction

The predominant method of gold extraction in the gold mining industry involves cyanidation of an ore under aerated conditions to form $Au(CN)_2^-$. Under such conditions, sulfides and base metals can form thiocyanate and metallo–cyanide complexes. The cyanidation of cupriferous minerals creates several problems, the foremost of which results from the large cyanide losses incurred due to complexation of the cyanide-soluble copper. Since cyanide is the most expensive reagent in the process, these losses can render the cyanidation process uneconomical. The Cu(I) cyanide complexes formed during cyanidation can subsequently foul the activated carbon used to recover the $Au(CN)_2^-$ from the leachate in

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the carbon-in-leach (CIL) process. This fouling can be minimised by the addition of further cyanide to the leachate to prevent the formation of the dicyano Cu(I) complex, which is very strongly adsorbed on the activated carbon to the point that it can prevent adsorption of the Au(I) complex. Finally, the large concentrations of Cu(I)–cyanide complexes in the final effluent passed to the tailings dams can pose a significant environmental hazard, depending on the location of the gold mine.

The mining of cupriferous gold ore deposits is becoming increasingly frequent. It is considered that, on a global basis, copper minerals are the second largest consumer of cyanide in the gold cyanidation process [1]. The developments described in this paper were undertaken at both the University of Tasmania and the Telfer Gold Mine (TGM) in Western Australia over a two year period. The TGM is located in the Great Sandy Desert, Western Australia and is one of the most geographically isolated mining centres in Australia. At several stages in its 20 year history, Telfer has been one of the largest gold mines in Australia. The most commonly occurring cupriferous mineral found at Telfer is chalcopyrite ($CuFeS_2$), with chalcocite (Cu_2S) and malachite ($CuCO_3$–$Cu(OH)_2$) also being found in the ore body.

The effect of the cyanide soluble copper minerals on the leaching process has received considerable attention over the years and several excellent reviews have been published [2,3]. Early workers [4] reported that chalcopyrite was only marginally soluble in dilute sodium cyanide solutions, while malachite and chalcocite were almost completely dissolved. However, the solubility of these cupriferous minerals, and in particular chalcopyrite, was affected by various other factors such as the degree of oxidation of the mineral, particle size and cyanide concentration. Consequently, the amount of cyanide-soluble copper minerals present in an ore body can vary over a considerable range and this may restrict the feasibility of mining a particular ore body. Several new processes have been developed to cope with this increasingly common problem [5,6], many of which require careful control of the CN:Cu molar ratio, *R*, since this ratio governs the gold leaching kinetics. It has been established [4] that the leaching kinetics are very slow when *R* is less than 3 and that there is no significant increase in the leaching kinetics when *R* exceeds 4. In view of this, the optimum value for *R* would appear to lie between 3 and 4.

The determination of *R* using standard methods is not a simple task as both cyanide and copper must be determined separately. Copper is routinely determined by atomic absorption spectroscopy (AAS), and the most common means of cyanide determination is the use of an argentometric titration. However, this method suffers from a significant positive interference from the Cu(I)–cyanide complexes due to the kinetically labile cyanide ligands in these complexes [1]. The interference from the Cu(I)–cyanide complexes can be removed by acid distillation of the sample to liberate HCN, with subsequent collection of cyanide in a hydroxide solution, but this is a lengthy procedure requiring considerable operator attention. Cyanide, thiocyanate and the metallo–cyanide complexes have been determined successfully in gold cyanidation leachates with HPLC instrumentation using ion chromatographic (IC) methods [7]. Ion interaction reversed-phase chromatography has been the most commonly used separation technique for the metallo–cyanide complexes and involves separation on a reversed-phase silica column with an aqueous eluent containing a quaternary ammonium salt and various organic solvents (usually acetonitrile) [7]. The metallo–cyanide complexes have generally been detected using a UV absorbance detector. Thiocyanate can also be separated and detected with the same conditions used for the metallo cyanide complexes, but cyanide is unretained in the above separation and is also UV transparent. Cyanide has been detected in this separation by either pre-column derivatisation with Ag to form $Ag(CN)_2^-$ [8] or by post-column derivatisation with a selective colorimetric reaction to produce a visible dye [9]. This PCR also derivatised the CN groups present in thiocyanate and the cyanide complexes of Cu(I) and Ag(I).

The above PCR was used to study the partial dissociation of the Cu(I)–cyanide complexes during the separation of these species by ion-interaction reversed-phase HPLC [10]. This partial dissociation resulted from the equilibrium perturbations that occurred during the chromatographic separation and the kinetic lability of the cyanide ligands. The composition of the eluted Cu(I)–cyanide peak was

found to be independent of the sample injected onto the column and could be altered by the addition of cyanide to the eluent. The addition of cyanide to the eluent reduced on-column dissociation of the Cu(I)–cyanide complexes, thereby improving the peak shape and increasing the retention time of the Cu(I)–cyanide peak. The amount of cyanide that could be added to the eluent was limited by the effect on the PCR detector response since the signal:noise ratio decreased as the cyanide concentration in the eluent was increased. Two important practical applications to the analysis of gold cyanidation leachates were suggested by the above study. The first concerned the determination of the CN:Cu(I) molar ratio (*R*) in cyanide leachates, which is important for the reasons mentioned earlier. The second concerned the accurate determination of thiocyanate and Cu(I)–cyanide complexes, both of which are commonly found in cyanide leachates. It has been previously reported that thiocyanate interfered in the chromatographic determination of Cu(I)–cyanide complexes [11].

This paper reports the further development of IC methods suitable for monitoring the gold cyanidation process, especially when cupriferous minerals are present in the ore body. In particular, IC methods suitable for the rapid determination of the CN:Cu molar ratio in gold cyanidation leachates are reported.

2. Experimental

2.1. Instrumentation

The HPLC instrument has been described previously [9,10] and consisted of a Waters (Milford, MA, USA.) M510 isocratic HPLC pump, a Waters 717 auto-sampler, a Waters M486 variable wavelength absorbance detector and a PCR detection system. The PCR system consisted of two Eldex pumps, two stitched open tubular reactors, a Waters column heater to maintain the reactors at a constant temperature (40°C) and a photometric detector operated at 436 nm. The first reactor was a coil 1.5 m in length with an I.D. of 0.030 mm. The second reactor initially consisted of three 5 m coils with an I.D. of 0.030 mm, connected in series, but was later replaced with a single 5 m coil with an I.D. of 0.050 mm. The reaction coils were prepared using the method described by Lillig and Engelhardt [12]. The PCR detector was a Waters M441 fixed-wavelength absorbance detector operating at 436 nm.

2.2. Preparation of the eluents

All the reagents used in this work were obtained from Aldrich (Castle Hill, Australia), unless otherwise stated. Acetonitrile was obtained either from Ajax Chemicals (Sydney, Australia) or from Merck (Kilsyth, Australia). Eluents were prepared with water from either a Milli-Q water purification system (Millipore, MA, USA) or from a Milli-RO water purification system. The ion-interaction reagent (IIR) used in the eluents was either Low UV PIC A (Waters) or was prepared from tetrabutylammonium hydroxide (TBAOH), KH_2PO_4 and H_2SO_4. NaCN (0–160 μ*M*) was added to the eluents. The composition of the final eluent was acetonitrile–water (25:75, v/v), TBAOH (10 m*M*), KH_2PO_4 (10 m*M*), H_2SO_4 (5 m*M*) and NaCN (80–160 *M*, added last to avoid release of HCN), adjusted to pH 8 with NaOH. All eluents were filtered (0.45 μm) and degassed under vacuum in an ultrasonic bath prior to use.

2.3. Preparation of the PCR reagents

The two PCR reagents were prepared as described below, filtered (0.45 μm) under vacuum prior to use each day, and stored in the dark at less than 4°C.

2.3.1. Reagent 1

N-chlorosuccinimide (0.15%, w/v) was added to a succinate buffer (0.1 *M*, pH 5.6) containing succinimide (3%, w/v).

2.3.2. Reagent 2

This final reagent contained the sodium salts of isonicotinic acid (INA) (230 m*M*), barbituric acid (BA) (15.6 m*M*) and EDTA (54 m*M*) and was prepared by dissolving the INA and BA in excess NaOH prior to the addition of Na_2EDTA. The final reagent pH was 7.2.

2.4. Standard solutions

Cyanide standards were prepared from a 0.1 *M*

stock solution of NaCN in 0.1 *M* NaOH. A Cu(I)–cyanide stock solution (0.1 *M*) was prepared from CuCN and NaCN in a 0.1 *M* NaOH solution, such that the CN:Cu molar ratio of this stock solution was 3.0. These solutions were kept alkaline to improve their stability. The copper concentration in the Cu(I)–cyanide stock solution was checked using AAS, while the cyanide concentration was checked by total cyanide distillation. Both the copper and cyanide concentrations were within 1% of expected values. The Cu(I)–cyanide standards used for analysis were prepared from the stock solutions of Cu(I)–cyanide and NaCN. Thiocyanate standards were prepared from a 0.1 *M* stock solution of KSCN. Both the NaCN and KSCN 0.1 *M* stock solutions were standardised potentiometrically with a standardised $AgNO_3$ solution. Other metal cyanide complexes were used as received. The study of the cobalt cyanide species was conducted using $CoCl_2$–$6H_2O$ (AnalaR grade, BDH, UK) and NaCN.

2.5. Operation of the instrument

Separations were performed on either a 50×3.9 mm I.D. or a 150×3.9 mm ID Waters Nova-Pak C_{18} analytical cartridge column fitted with a Waters guard column. The eluents were pumped through the column at a flow-rate of 1.0 ml/min. The UV absorbing metallo–cyanide complexes were detected immediately after elution from the column with a variable-wavelength detector set at an appropriate wavelength between 205 nm and 245 nm. The wavelength was changed to adjust the sensitivity of the detector.

The PCR comprised three reactions and two reagent additions. The first reagent contained a chlorinating reagent (*N*-chlorosuccinimide) to enable formation of CNCl. A pyridine derivative (isonicotinic acid) in the second reagent combined with the CNCl to form an aldehyde. An in situ condensation reaction then occurred between the aldehyde and barbituric acid to form an intermediate polymethine dye product with a λ_{max} of 515 nm. This polymethine dye further reacted with barbituric acid at a considerably slower rate to form a second polymethine dye with a λ_{max} of 600 nm. A large excess of isonicotinic acid was used since it has been shown that this stabilises the intermediate polymethine dye [13]. The flow-rates of the first and second PCR reagent pumps were approximately 0.1 and 0.2 ml/min, respectively. The derivatised cyanide and Cu(I)–cyanide peaks were detected after the PCR unit with a fixed wavelength detector operated at 436 nm.

3. Results and discussion

3.1. Selection of separation conditions

In order to improve the separation of the metallo–cyanide complexes from that previously reported, three factors influencing the separation were examined. These factors were the column length, concentration of the tetrabutylammonium cation (TBA^+) and the nature and concentration of the counter anions in the ion-interaction reagent (IIR). The last factor has been shown to have a significant effect on the retention of the metallo–cyanide complexes [11,14–17].

Several authors have used the proprietary IIR, Waters Low UV PIC A, for preparing eluents [9,10,18–20]. Fig. 1 illustrates the separation achieved using this reagent in an eluent comprising 25% acetonitrile, 5 m*M* low UV PIC A and 75 μ*M* NaCN. It should be noted that the Fe(III) and Ni(II) complexes had almost identical retention times under these separation conditions. An ion chromatographic analysis of a 5 m*M* solution of Low UV PIC A revealed the presence of both sulfate (5 m*M*) and phosphate (10 m*M*) as counter-anions. Several different combinations of these anions with TBA^+ were investigated as a means to vary separation selectivity. In view of the practical requirements of the separation as a tool for process monitoring, the separation requirements were as follows:

1. Complete resolution of thiocyanate and the Cu(I) complex. It should be noted that the eluted peak assigned to the Cu(I) complex actually consists of a stable mixture of the *di*-, *tri*- and *tetra*cyano complexes, with the actual composition being determined by the level of cyanide present in the eluent [10]. In the interests of simplicity, the term Cu(I) complex will be used to represent this mixture.
2. The concentration of cyanide in the eluent should

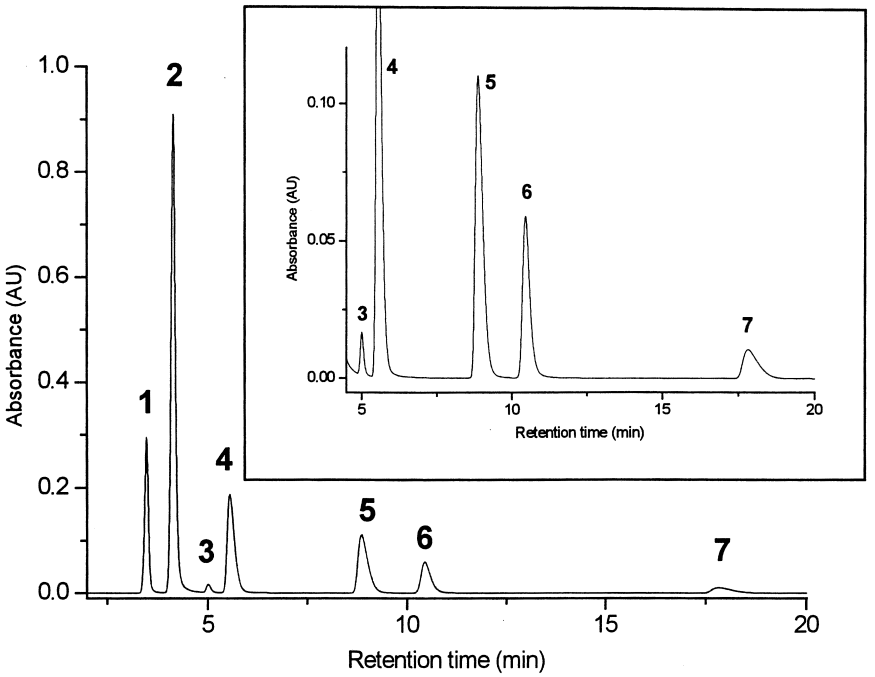

Fig. 1. UV detector (214 nm) chromatogram showing separation of standards of thiocyanate and six metal cyanide complexes. Peaks: (1) SCN; (2) Cu(I); (3) Ag; (4) Fe(II); (5) Co(III); (6) Ni(II); (7) Au(I) 15 cm Nova-Pak C_{18} column. Eluent: 25% acetonitrile, 5 m*M* Low UV PIC A, 75 μ*M* NaCN; pH=8.0.

be kept as low as possible to enable use of the cyanide PCR detection system.

3. Rapid analysis of mixtures containing SCN, Cu(I) and Fe(II).
4. Rapid analysis for the Au(I)–cyanide complex.

Due to the disparity in concentrations of the above analytes in the TGM samples, a small injection volume (typically 1–10 μl) was required for the analysis of cyanide, thiocyanate and the Cu(I)– and Fe(II)–cyanide complexes in the CIL process samples, while a large injection volume (50–100 μl) was required for analysis of the Au(I) complex.

Since thiocyanate and the Cu(I) and Fe(II) complexes have previously been eluted within 10 min on a 15 cm column [9], the first requirement was to reduce the retention time of the Au(I) complex. This could be achieved by use of a mobile phase with a higher acetonitrile concentration (e.g. 29%) or by increasing the concentration of the IIR counter-anion [16]. However, an alternative was to use the same eluent with a shorter analytical column, as shown in Fig. 2 for a 5 cm Nova-Pak C_{18} cartridge column. The Au(I) complex was the last peak eluted, giving an analysis time of less than 10 min.

The effects of the IIR counter-anions and cyanide in the eluent were studied using eluents comprising 25% acetonitrile and 5 m*M* TBAOH at a pH value of 7.95±0.05. Tables 1 and 2 show retention data for both the 15 cm and 5 cm columns under a range of eluent conditions, together with values for the resolution of thiocyanate and Cu(I) on the 15 cm column (Table 1). Low concentrations (<100 μ*M*) of cyanide were added to the eluent to improve the Cu(I) peak shape and increase the retention of the Cu(I) complex with respect to thiocyanate by in situ complexation. It has been shown previously that this in situ complexation of the Cu(I) complex increases both peak homogeneity and the average charge of the eluted Cu(I) complex [10]. It was necessary to have a suitable buffer in the eluent to minimise damage to the column by the alkaline samples. A phosphate buffer was selected as it has been used previously in this separation [8] and displays virtually no absorption at the detection wavelengths used in this work.

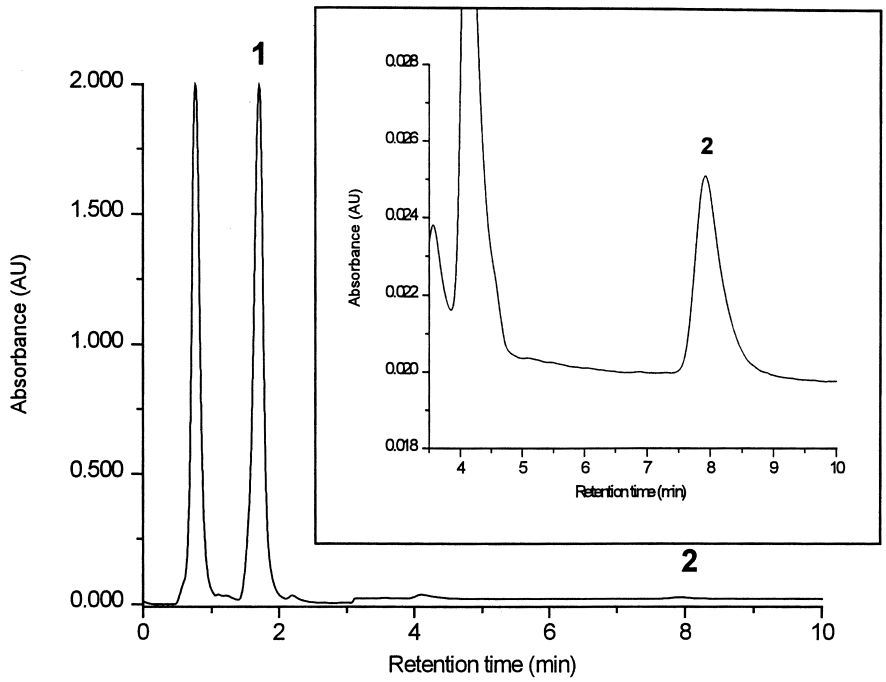

Fig. 2. UV detector (205 nm) chromatogram of a CIL sample showing rapid elution of the Au(I) complex on a 5 cm Nova-Pak C_{18} cartridge column. Concentration of Au(I) complex = 1.32 ppm Peaks: (1) Combined SCN and Cu(I) peaks; (2) Au(I). Injection volume 50 μl. Eluent: 25% acetonitrile, 5 m*M* TBAOH, 10 m*M* KH_2PO_4, 10 m*M* Na_2SO_4, 80 m*M* NaCN; pH = 8.0.

Table 1
Retention data obtained on a 15 cm column (each eluent contained 25% acetonitrile and the first five eluents contained 5 m*M* TBAOH; the final eluent pH was 7.95±0.05)

[Phosphate] (m*M*)	[Sulfate] (m*M*)	[Cyanide] (μ*M*)	Retention time (min)					Resolution of SCN and Cu(I)
			SCN	Cu(I)	Fe(II)	Fe(III)	Au(I)	
10	0	40	4.35	5.00	–	–	–	2.21
10	10	80	3.70	4.02	3.85	9.13	–	1.25
8.3	5.0	40	3.52	3.83	6.51	11.38	18.18	1.30
5.0	3.0	60	4.07	4.93	17.05	>20	–	2.94
5.0	5.0	60	3.95	4.62	12.41	17.73	21.89	2.41
5.0 m*M* low UV PIC A		75	3.47	4.14	5.55	–	17.82	2.50

Table 2
Retention data obtained on a 5 cm column (each eluent contained 25% acetonitrile and the first five eluents contained 5 m*M* TBAOH; the final eluent pH was 7.95±0.05)

[Phosphate] (m*M*)	[Sulfate] (m*M*)	[Cyanide] (μ*M*)	Retention time (min)				
			SCN	Cu(I)	Fe(II)	Fe(III)	Au(I)
10	0	40	–	–	4.63	6.31	9.02
10	10	80	–	–	1.53	3.29	7.90
5.0	5.0	60	–	–	4.33	6.49	8.73
5.0	7.0	60	–	–	2.73	4.84	8.23
5.0 m*M* low UV PIC A		0	–	–	2.00	3.52	7.46

The first eluent shown in Tables 1 and 2 (comprising 10 m*M* phosphate buffer and 40 μ*M* cyanide) gave broad peaks and incomplete separation of the Fe(II) and Fe(III) complexes. Previous studies have shown that the addition of sulfate to the eluent improved the peak shape of the metallo–cyanide complexes [21]. Consequently, the effects of sulfate in the eluent were investigated and significant changes in the retention times, particularly those of the Fe(II) and Fe(III) complexes, were noted. This was attributable to the −3 and −4 charges on the Fe(III) and Fe(II) complexes, respectively, compared to the −1 charge on thiocyanate and the Au(I) complex and the variable charge of between −1 and −2 for the Cu(I) complex, depending on the concentration of cyanide in the eluent [10]. High analyte charge results in an increased negative slope of a plot of log k' versus log [counter-anion] [17]. After consideration of peak shape, separation time and resolution of the various analytes, the optimal concentrations of counter-anions in the eluent were found to be 10 m*M* phosphate buffer, 5 m*M* sulfate and a cyanide concentration adjusted to suit the particular sample.

In view of the desirability of using the 5 cm column because of the rapid analyses possible, further optimisation of the eluent used with this column was undertaken by varying the percentage of acetonitrile and the concentration of TBA^+. Table 3 shows retention data for a range of eluent compositions, all of which contained phosphate and sulfate at the optimal levels determined above. Increasing the TBA^+ or cyanide concentrations, or decreasing the percentage of acetonitrile, were found to improve the resolution of thiocyanate and Cu(I). The optimal eluent composition was 25% acetonitrile, 10 m*M* TBAOH, 10 m*M* KH_2PO_4, 5 m*M* H_2SO_4 and 160 μ*M* NaCN, adjusted to pH 8.0. The separation of a CIL sample with this eluent is shown in Fig. 3. It is noteworthy that the elution order differed to that obtained in previous studies using an eluent containing 5 m*M* low UV PIC A in that the Au(I) complex which had previously been eluted last was now eluted prior to Fe(III) (not shown in Fig. 3). Again, this can be attributed to the effects of counter-anions on the elution of the highly charged Fe(III) complex.

3.2. Modifications to the PCR detection system

The PCR detection system consisted of two reagents and their delivery pumps, two reactors and a visible wavelength absorbance detector. The PCR reaction used was a variant of the Konig reaction [22] which is a selective reaction generally used for determining ppb levels of cyanide. Modifications to this detection system were implemented to facilitate good linearity and precision for cyanide in the concentration range present in the process samples under study, namely 1–10 m*M*. Negative interferences in the PCR reaction have been reported for reduced anions such as sulfide, sulfite and nitrite, with the most significant interference being caused by sulfide [23]. However, it should be noted that samples obtained from a gold cyanidation process are usually aerated and contain large concentrations of cyanide. Under these conditions, it is unlikely that significant concentrations of reduced species would exist for any extended period of time. In addition, sulfur species such as sulfide or sulfite would react with cyanide to form thiocyanate [24]. Earlier work had shown that the PCR detection system used in

Table 3
Retention data obtained on the 5 cm column using mobile phases with varying amounts of acetonitrile, TBAOH and cyanide

[MeCN] (%)	[TBA^+] (m*M*)	[PO_4] (m*M*)	[SO_4] (m*M*)	[CN] (m*M*)	Retention time (min)				Resolution of SCN and Cu(I)
					SCN	Cu(I)	Fe(II)	Au(I)	
23	5	10	5	80	–	–	4.03	10.03	–
25	7	10	5	80	1.58	1.87	3.17	7.72	1.81
25	8	10	5	80	1.67	2.00	3.57	–	2.05
25	8	10	5	160	1.65	2.07	3.63	–	2.63
25	9	10	5	160	1.70	2.18	3.93	8.62	2.88
25	9	10	5	0	1.72	1.93	3.88	8.75	Not resolved
25	10	10	5	160	1.78	2.32	4.40	9.07	3.01

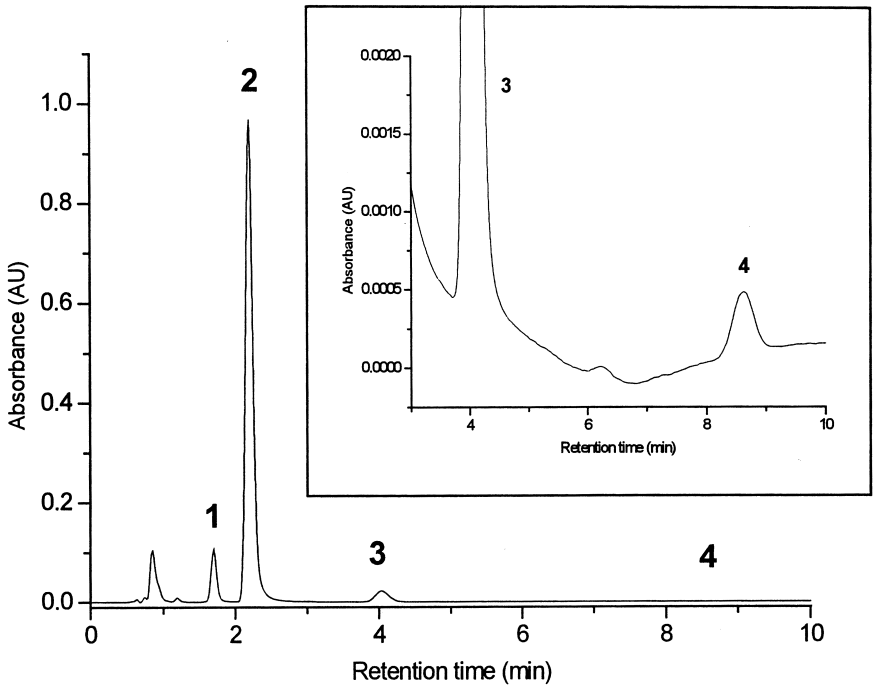

Fig. 3. UV detector (225 nm) chromatogram of a CIL sample analysed on a 5 cm Nova-Pak C_{18} column. Peaks: (1) SCN; (2) Cu(I); (3) Fe(II); (4) Au(I) Sample concentrations (ppm): SCN (27.5); Cu(I) (103); Fe(II) (1.5); Au(I) (1.2). Injection volume: 10 μl. Eluent: 25% acetonitrile, 10 m*M* TBAOH, 10 m*M* KH_2PO_4, 5 m*M* Na_2SO_4, 160 μ*M* NaCN; pH = 8.0.

this work could tolerate up to 500 ppm sulfide before interference was observed [9]. The reason for the large tolerance towards sulfide may be due to the slight retention of cyanide, enabling separation from the void volume (and, therefore, from sulfide, which is unretained and is eluted with the void volume) at lower concentrations.

The first step in the PCR reaction involves the chlorination of cyanide to form cyanogen chloride. This is a very rapid reaction [25–27] and the cyanogen chloride produced subsequently undergoes rapid hydrolysis in the presence of a chlorination reagent. This hydrolysis is base catalysed and accelerated in the presence of excess chlorine [28]. Consequently, to avoid loss of CNCl, it is important that the residence time in the first reactor is small and that the concentration of the chlorinating reagent is not excessive. *N*-Chlorosuccinimide (NCS) was selected as the chlorination reagent for this work since it has been reported that this reagent can be stabilised by the addition of a 10-fold excess of succinimide [29]. However, the results obtained in this and our earlier work [9] did not show the expected degree of stability reported for the NCS reagent. Alternative chlorination reagents, (hypochlorite and chloramine-T) were examined but were not significantly more stable than the NCS reagent. In addition, hypochlorite was found to have a detrimental effect on the pump seals, while the chloramine-T reagent was not soluble over the range of pH values required for the PCR system. It was, therefore, decided to continue using the NCS reagent and to freshly prepare the reagent every 1–2 days and to keep the NCS reagent bottle shielded from light and packed with ice in an insulated container. Using this arrangement the temperature of the NCS reagent could be maintained at less than 4°C for 24 h. It was also found that increasing the NCS concentration from 0.10% (w/v) to 0.15% (w/v) improved its stability over a 2 day period. The drift in a series of cyanide calibration plots prepared from NaCN standards analysed at intermittent intervals over the course of a 12 h period is shown in Fig. 4. After 2 days the cyanide calibrations became

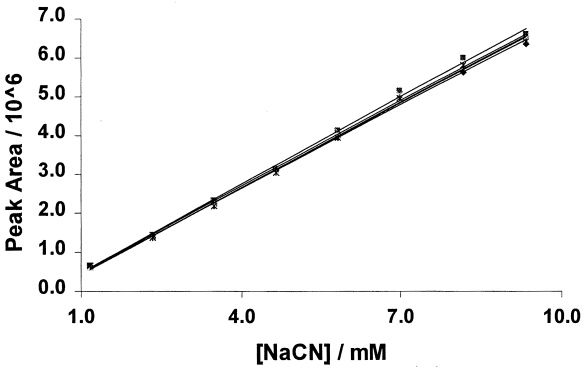

Fig. 4. Variation in cyanide calibrations over a 12 h period. Injection volume: 10 μl. PCR Reactor 2: 5 m×0.030 mm I.D. stitched reaction coil with a residence time of 19 s. PCR reagent 2: 0.23 *M* INA, 15.6 m*M* BA, 2% Na_2EDTA. Other PCR conditions as described in Section 2. 5 cm Nova-Pak C_{18} column. Eluent: 25% acetonitrile, 10 m*M* TBAOH, 10 m*M* KH_2PO_4, 5 m*M* H_2SO_4, 160 μ*M* NaCN; pH=8.0.

noticeably non-linear at higher cyanide concentrations due to a marked decrease in the oxidising potential of the NCS reagent. To facilitate rapid preparation of the NCS reagent, a stock solution containing succinate buffer (0.1 *M*, pH 5.6) and succinimide (3.0%) was prepared. *N*-Chlorosuccinimide (0.15%) was dissolved in this stock solution on a daily basis and filtered to produce the desired NCS reagent.

The second PCR reagent solution contained both isonicotinic acid (INA) and barbituric acid (BA), these being selected from the many options available because they are relatively non-toxic, easily prepared and stable for a period of weeks when kept at <4°C and shielded from light. The cyanogen chloride produced in the first step of the PCR reaction attacks the nitrogen in the pyridine ring, resulting in ring opening and subsequent formation of a reactive dialdehyde. One of the aldehyde groups then undergoes a condensation reaction with the coupling reagent. Initially one molecule of the coupling reagent reacts with one of the aldehyde groups to rapidly form an intermediate polymethine dye. The remaining aldehyde group in this intermediate dye will subsequently undergo a second, slower condensation reaction with another molecule of barbituric acid to form a final dye. Several authors have utilised this intermediate dye for the photometric determination of cyanide in FIA [30–32] and HPLC-PCR [9,33]. Formation of the intermediate dye is favoured by a 100-fold excess of INA over the coupling reagent (BA) [13].

The λ_{max} observed for the intermediate INA/BA dye in our work was 515 nm, which is in contrast to other papers that have reported 525–527 nm [31,34]. This difference can be attributed to the solvent effect of acetonitrile in the reaction mixture. The acetonitrile concentration in the effluent from the PCR detection system was calculated to be 19% for an eluent concentration of 25%. In order to decrease the sensitivity of this method so that it could be utilised for the anticipated levels of cyanide in the process samples, two detection wavelengths (436 and 546 nm) accessible to a fixed wavelength detector were examined. Of these, the 436 nm wavelength was selected because of the good linearity of the calibration curve at higher concentrations of cyanide.

Three reaction times in the second reactor were examined: 19, 37 and 56 s. These reactions times were achieved by the use of three knitted 5 m×0.30 mm I.D. reaction coils. It was observed that there was a large increase in the PCR absorbance when the reaction time was increased from 19 to 37 s, while a relatively small increase occurred when the reaction time was increased to 56 s. This indicated that formation of the intermediate dye was almost complete after 56 s. Kuban [31] reported a reaction time of 120 s for formation of the intermediate dye when using the INA/BA reagent, but the temperature used was not stated. We have found that a reaction temperature of 40°C is optimal for the INA/BA reaction. The INA and BA concentrations were optimised to provide the best calibration linearity using the above reaction conditions and a detection wavelength of 436 nm. The final INA and BA concentrations selected were 230 m*M* and 15.3 m*M*, respectively. Good calibration linearity for 1–9 m*M* NaCN was achieved using a reaction time of 19 s, but increasing the reaction time to 56 s reduced the linearity range to 1–7 m*M* NaCN due to the large absorbance values generated with the longer reaction time.

After several problems were experienced using the three 5 m×0.30 mm I.D. reaction coils, the second reactor was replaced with a 5 m length of 0.50 mm I.D. stitched PFTE tubing reactor. The residence time

in this new reactor was 47 s and the back pressure generated by the PCR unit was considerably reduced, thereby improving the signal:noise ratio for cyanide.

3.3. Determination of the CN:Cu molar ratio

When a series of Cu(I)–cyanide standards with equimolar copper concentration and increasing CN:Cu molar ratios, *R*, was injected onto the ion-interaction separation system, two peaks were observed with the PCR detector, as shown in Fig. 5. The first peak was due to free cyanide in the sample, together with any further free cyanide produced by dissociation of the Cu(I) complex during its passage through the chromatographic column. The second peak was due to the derivatisation of cyanide in the Cu(I) complex. The peak area of the Cu(I) peak did not change with the value of *R* in the injected sample, while the cyanide peak increased almost proportionally with *R* as shown in Fig. 6A. We have shown previously [10] that under constant eluent conditions, the composition of the eluted Cu(I) peak was constant, regardless of the composition of the injected sample. Consequently, the CN:Cu(I) peak

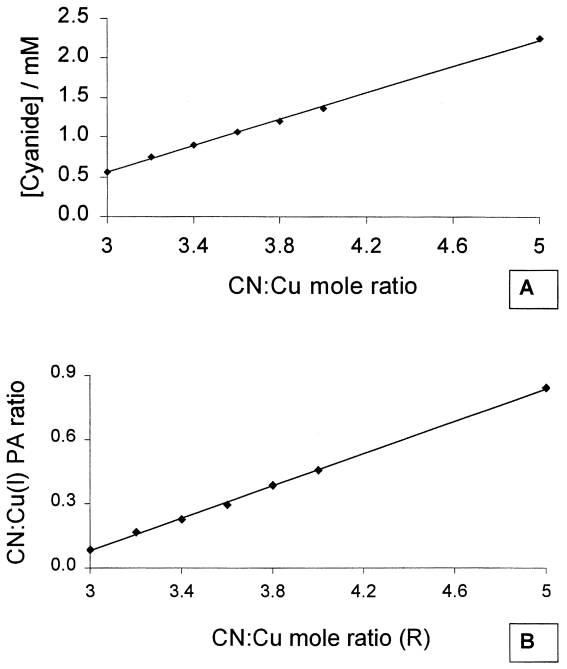

Fig. 6. (A) Cyanide concentration in the CN peaks for each Cu(I) standard shown in Fig. 5. (B) CN:Cu(I) peak area (PA) ratio as a function of the CN:Cu(I) molar ratio (*R*) for each Cu(I) standard shown in Fig. 5.

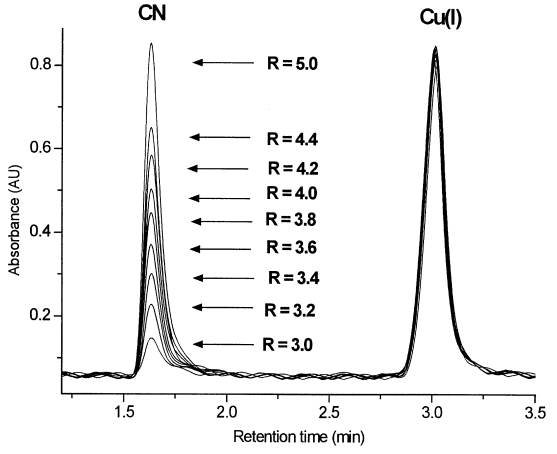

Fig. 5. PCR detector chromatograms of a series of 1 m*M* Cu(I)–cyanide standards with the CN:Cu mol ratio, *R*, varying from 3.0 to 5.0. PCR conditions: three 5 m×0.030 mm I.D. stitched reaction coils with a residence time of 57 s. PCR reagent 2: 0.23 *M* INA, 15.6 m*M* BA, 2% Na_2EDTA. Other PCR conditions as described in Section 2. Injection volume: 10 μl Column: 5 cm Nova-Pak C_{18}. Eluent: 25% acetonitrile, 10 m*M* TBAOH, 10 m*M* KH_2PO_4, 5 m*M* H_2SO_4, 80 μ*M* NaCN; pH=8.00.

area ratio was a direct reflection of the CN:Cu(I) molar ratio of the sample injected onto the column, as shown in Fig. 6B. When the plot shown in Fig. 6B was extrapolated to a peak area ratio of zero, the intercept on the *R* axis indicated that the CN:Cu molar ratio of the eluted Cu(I) peak was 2.79 under the chromatographic conditions used.

The concentration of cyanide in the cyanide and Cu(I) peaks was determined using a calibration of NaCN standards. For a 1 m*M* Cu(I)–cyanide standard with a CN:Cu molar ratio of 4.0, the concentrations of cyanide in the free cyanide and Cu(I) peaks was found to be 1.18 and 2.78 m*M*, respectively, providing a total cyanide concentration of 3.96 m*M*, which compared very well with the expected total cyanide concentration of this standard (4.0 m*M*). Since the concentration of the Cu(I)–cyanide standard injected onto the column was 1 m*M*, the CN:Cu molar ratio of the eluted Cu(I) peak was 2.78, which compared very favourably with the CN:Cu molar ratio (2.79) found from extrapolation

of the CN:Cu calibration plot as discussed above. It was also reasoned that use of the peak area ratio would eliminate errors from long term drifts in the PCR detection system.

A new process involving the cyanide leaching of copper–gold ore containing a high copper concentration was undergoing trials during the period that the HPLC instrument was located at TGM. This leaching operation required the CN:Cu molar ratio to be monitored over a period of several months and was thus an ideal application for the HPLC instrument. The leachate typically contained between 2000 and 4000 ppm Cu as the Cu(I) complex, together with low concentrations of thiocyanate and the complexes of Co(III), Fe(II), Ni(II) and Au(I). An injection volume of 10 μl of a 40-fold dilution of the leachate was initially used, but this was later replaced with an injection volume of 1.0 μl of a 4-fold dilution of the leachate.

3.4. Analysis of Cu(I)–cyanide leachate

The final eluent developed in Section 3.1 allowed the separation of thiocyanate and the Cu(I) complex on a 5 cm column, and these chromatographic conditions were initially used to analyse the leachate. Since the thiocyanate concentration in these samples was very low, it was possible to reduce the NaCN concentration in the eluent from 160 to 80 μ*M* and still achieve baseline resolution of thiocyanate and Cu(I) peaks. The slope of the calibration plot for the CN:Cu(I) molar ratio in the eluent containing 80 m*M* NaCN was identical to that for the eluent containing 160 μ*M* NaCN, but as expected gave a smaller *R* value for an extrapolated peak area ratio of zero. The UV detector chromatogram (which provided speciation of the metallo–cyanide complexes and thiocyanate) revealed that the large concentration of Cu(I) complex in these samples resulted in partial co-elution of the Cu(I) and Fe(II) peaks. For this reason it was necessary to use a 15 cm analytical column to enable separation of thiocyanate and all the metallo–cyanide complexes when the level of Cu(I) was very high. A chromatogram for such a sample is shown in Fig. 7 using an eluent containing 150 m*M* NaCN and programmed changes of detection wavelength to maximise detection sensitivity. Complete separation of all species was obtained.

3.5. Effect of Cu(I) concentration on determination of R

The effect of Cu(I) concentration on the CN:Cu molar ratio calibration plot was determined for the eluent containing 80 μ*M* NaCN. This was performed on a series of Cu(I)–cyanide standards with the Cu(I) concentration ranging from 0.6 to 1.4 m*M*, but all having a CN:Cu molar ratio of 3.0. The peak area ratios and percentage variation from the 1.0 m*M* Cu(I) standard are shown in Table 4, from which it can be noted that a variation of less than 2% was observed for solutions containing Cu(I) in the range 0.8–1.4 m*M*. This permitted a CN:Cu molar ratio calibration prepared with standards containing a single Cu(I) concentration to be used for solutions containing varying amounts of Cu(I). It was found that increasing the NaCN concentration in the eluent increased the range of Cu(I) concentrations that could be analysed using the same calibration plot. A calibration plot prepared using 15 m*M* Cu(I) standards (1.0 μl injection volume) and an eluent containing 140 μ*M* NaCN was found to be applicable for sample solutions containing Cu(I) in the range 7.5–22.5 m*M*. This is illustrated in Table 5 which shows CN:Cu values obtained for a series of standards using calibration plots derived from either a single 15 m*M* Cu(I) concentration or a series of Cu(I) concentrations. The values obtained using each approach were very similar. From these results it was evident that only five standard solutions (Nos. 1–3, 9 and 10 in Table 5) were required for calibration plots for determination of the CN:Cu molar ratio and the concentrations of the Cu(I) complex and thiocyanate in the samples.

3.6. Analysis of samples with CN:Cu molar ratios < 3.0

Two approaches were investigated for samples having *R* values below 3.0. The first was to extrapolate the calibration plot for the CN:Cu molar ratio, which was applicable only when a positive cyanide peak was obtained. However, very small cyanide peaks were difficult to determine accurately due to the baseline pump noise in the PCR detector chromatograms. Injection of a sample with a CN:Cu molar ratio below the intercept value for the cali-

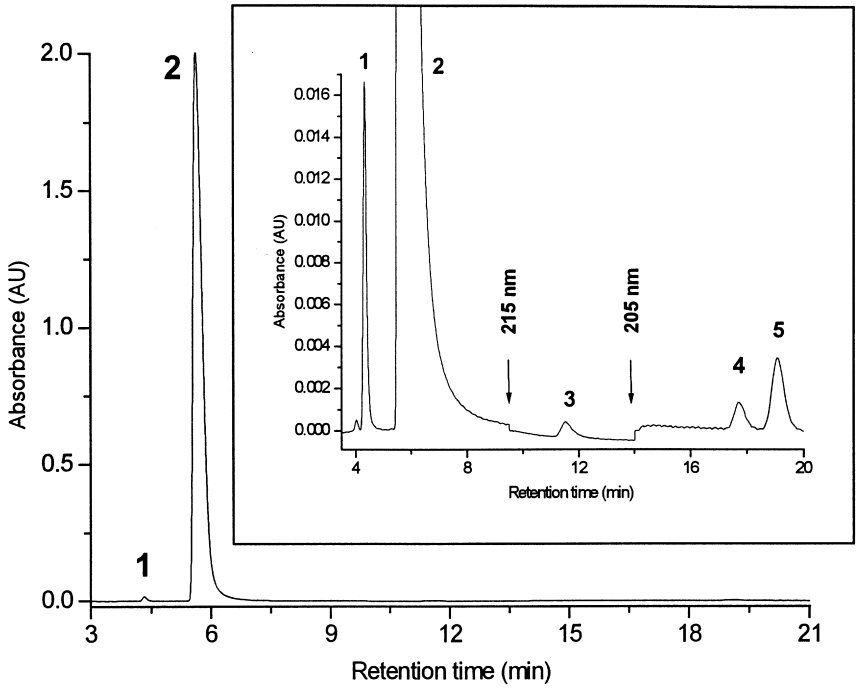

Fig. 7. Cu(I)–cyanide leach sample analysed on a 15 cm column. Peaks: (1) SCN; (2) Cu(I); (3) Fe(II); (4) Ni(II); (5) Co(III). Sample concentrations: SCN (94.4 ppm); Cu(I) (4616 ppm); Fe(II), Ni(II) and Co(III) (<1 ppm). Eluent: 25% acetonitrile, 10 m*M* TBAOH, 10 m*M* KH_2PO_4, 5 m*M* H_2SO_4, 150 m*M* NaCN; pH=8.0. Injection volume: 1.0 μl. Undiluted sample. UV absorbance detector: Programmed wavelength changes: $t=0$ min, $\lambda=230$ nm; $t=9.5$ min, $\lambda=215$ nm; $t=14.0$ min, $\lambda=205$ nm.

bration plot gave a negative cyanide peak due to removal of cyanide from eluent by the eluted Cu(I)–cyanide complex.

The second method for handling samples with low CN:Cu molar ratios was to perform standard additions of cyanide to the samples, after which the concentration of cyanide originally present in the sample could be calculated. When significant concentrations of other cyano species were present in the sample, it was necessary to account for changes to the peak areas of all species before and after the standard addition of cyanide. The validity of the standard addition procedure was tested on leachate samples having *R* values greater than 3.0 (i.e. those which fell within the normal calibration range of the proposed method). The experimentally determined *R* values after the NaCN addition were within 5% of the calculated values, as shown in Table 6. The standard addition procedure was applied successfully to samples obtained after the cyanidation of material

Table 4
Variation in CN:Cu(I) peak area ratio with concentration of Cu(I) in the sample (each sample had a CN:Cu molar ratio of 3.0; the eluent contained 80 m*M* NaCN and the analysis was performed on a 15 cm column)

[Cu] (m*M*)	CN:Cu(I) peak area ratio	% Variation in peak area ratio compared to 1 m*M* Cu(I) standard
0.6	0.0899	91.59
0.8	0.0978	99.63
1	0.0982	100.00
1.2	0.0969	98.65
1.4	0.1001	101.97

Table 5
Standards used for the determination of [Cu(I)], [SCN] and the CN:Cu molar ratio

Standard no.	[Cu] (m*M*)	CN:Cu mol ratio	[SCN] (ppm)	CN:Cu PA ratio	Calculated CN:Cu molar ratio	
					15 m*M* Cu stds.	Other Cu stds.
1	7.5	5.00	50	0.91	4.98	5.00
2	12	4.25	100	0.62	4.24	4.25
3	15	3.00	150	0.14	3.03	3.03
3	15	3.00	150	0.13	3.00	3.00
4	15	3.50	50	0.32	3.49	3.49
5	15	4.00	100	0.51	3.97	3.98
6	15	4.50	250	0.72	4.49	4.50
7	15	5.00	200	0.93	5.03	5.05
8	7.5	4.00	150	0.54	4.03	4.05
9	19.5	3.77	200	0.41	3.71	3.72
10	22.5	3.33	250	0.25	3.29	3.30

The CN:Cu peak area ratio (PA) was determined experimentally in an eluent containing 140 μ*M* NaCN and the CN:Cu molar ratios for each standard were then calculated from calibration plots prepared either from standards 3–7 or from standards 1–3, 8–10.

Table 6
Standard additions of NaCN to pyrite leach samples with $R>3$

Sample no.	[Cu] (ppm)	CN:Cu molar ratio		Recovery %
		Before standard addition	Calculated using standard addition	
1	7040	3.10	3.07	96.4
2	6621	3.16	3.15	99.0
3	6324	3.16	3.19	102.9
4	5388	3.60	3.64	103.4
5	5306	3.31	3.37	105.2

The *R* value of each sample was determined before and after the standard addition. The *R* value of the original solution was then calculated from the value determined after the standard addition. This calculated value was compared to the value determined before the standard addition and expressed as a percentage.

obtained from a pyrite flotation process containing up to 150 m*M* of Cu(I), 7 m*M* Fe(II) and 93 m*M* thiocyanate.

3.7. Interference from cobalt–cyanide complexes

Comparative determinations of Cu(I) in leachates using data from the UV and PCR detectors in the HPLC method and AAS showed a positive bias in the results from the UV detector (Table 7). On the other hand, agreement between the values obtained by the PCR detector and AAS was good, and the values for total cyanide obtained from the PCR detector and by acid distillation of the sample were

Table 7
Comparison of HPLC results for four samples with results obtained by standard methods (the total CN in the HPLC results was calculated as a product of the [Cu(I)] determined by the PCR detector and the CN:Cu mol ratio)

Sample	HPLC results				[Cu] by AAS (m*M*)	Total CN by acid digest (m*M*)	% difference
	[Cu(I)] (m*M*) UV detector	[Cu(I)] (m*M*) PCR detector	CN:Cu molar ratio	Total CN (m*M*)			
A	48.9	47.0	3.50	164	44.6	158	+4.43
B	46.6	43.6	3.16	138	41.2	137	+0.87
C	46.0	42.8	3.75	161	41.8	166	−3.40
D	46.0	42.2	3.76	159	42.1	164	−3.18

also in agreement. This suggested that there was an interfering species which was detectable at the UV wavelength but was not derivatised by the selective PCR reaction.

Analysis of the leachates showed the presence of cobalt and a peak due to Co(III) was evident in Fig. 7, together with a small, unidentified peak eluted just prior to thiocyanate. The reaction of Co(II) with cyanide is slow and the final product, $[Co(CN)_6]^{3-}$, is not formed immediately. Chromatographic analysis of a solution of NaCN added to Co(II) chloride gave a series of peaks, with two major peaks at retention times of 4.0 and 5.9 min. The first of these had the same retention time as the small, unidentified peak in Fig. 7, whilst the second had the same retention time as Cu(I). The chromatography of the cyano–cobalt complexes has previously been reported [35] and it has been shown that the first complex formed when cyanide was added to a Co(II) salt was the pentacyano cobalt(II) complex, $[Co(CN)_5]^{2-}$ (**I**). In the presence of oxygen (which is ubiquitous in a leaching process), (**I**) formed an oxygen bridged complex, $[Co(CN)_5CoOOCo(CN)_5]^{6-}$ (**II**), which reacted further with **I** to form the cobalt(III) pentacyano complex $[Co(CN)_5]^{3-}$ (**III**). Finally, **III** and cyanide reacted to form the hexacyanocobalt(III) complex, $[Co(CN)_6]^{3-}$ (**IV**). From our observations and the conclusions obtained by Thompsen [35], it would appear that the two major peaks noted above in the chromatogram of the mixture of NaCN and Co(II) chloride could be assigned to the intermediate Co–cyanide complexes **I** and **II**. This suggested that the positive bias in the UV detector results for Cu(I) may have been due to interference from one of the intermediate Co–cyanide complexes. Such a complex would be detectable at low UV wavelengths but would not be derivatised by the PCR reaction.

3.8. Validation of HPLC method

The results shown in Table 7 show that the difference between the HPLC method and standard method for determining total cyanide was less than 5%. To further confirm the validity of the HPLC method, a series of controlled leach tests was performed in which the initial amount of cyanide added to the ore sample was known accurately. The various cyano species formed during the leaching process were then determined by HPLC. Cyanide, thiocyanate and the metallo–cyanide complexes were determined by the methods developed in this paper, whilst cyanate was determined using a chromatographic method reported earlier [36]. The mass balance of all the cyano species produced during the leaching experiments was within 5% of the cyanide initially added to each leach test.

4. Conclusion

The proposed method allows the rapid and reliable determination of the CN:Cu molar ratio using ion-interaction reversed-phase HPLC. At the same time, the concentrations of thiocyanate and the metallo–cyanide complexes in the sample can also be determined. These analyses allow the total cyanide concentration distributed between the various cyano species to be measured. The major cyano species in the samples investigated required an analysis time of 12 min or less for each determination, but longer analysis times may be required for samples containing high concentrations of other species. The proposed methodology has been operated successfully under field conditions and will now be developed further as part of an on-line monitoring system for the cyanidation treatment of cupriferous and pyritic gold ores.

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