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Ion chromatographic analysis of cyanate in gold processing samples containing large concentrations of copper(I) and other metallo–cyanide complexes

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Abstract

An ion chromatographic (IC) method was developed for the determination of cyanate in gold cyanidation samples containing large concentrations of metallo–cyanide complexes. The analysis was performed on a Waters HC IC-Pak A anion-exchange column with an anthranilic acid eluent, with detection achieved using indirect UV at 355 nm. Two procedures were developed for removal of the metallo–cyanide complexes prior to the IC analysis. The first was a manual off-line method which used solid-phase extraction cartridges containing a strong anion-exchange resin to trap the complexes and to then enable determination of cyanate without interference. In the second approach, an automated on-line method was developed which used an anion-exchange guard column to trap the complexes and a column switching valve to allow backflushing of the cyanate from the guard column. This enabled the total analysis to be performed in a time of 10–14 min, depending on the sample composition. Finally, a comparison of results obtained by the standard Kjeldahl nitrogen method for cyanate and the IC method revealed an interference in the Kjeldahl method for samples containing large concentrations of Cu(I)–cyanide complexes.

Keywords: Cyanate; Metal–cyanide complexes; Copper(I)–cyanide

1. Introduction

Cyanide is generally the most expensive reagent in the gold cyanidation process. Unfortunately, during this process cyanide is lost from the leachate by various chemical routes, resulting in the formation of base metallo–cyanide complexes, thiocyanate and cyanate [1]. Cyanate is formed from the oxidation of cyanide. An important oxidation mechanism occurs during the cyanidation of cupriferous ores due to the reduction of Cu(II) with cyanide [2].

Cyanate is commonly determined using the Kjeldahl nitrogen method [3]. This method requires over 1 h per analysis and involves the boiling of concentrated acids. Ion chromatography (IC) has been successfully used for the determination of cyano species in cyanide leachates. Most of the important metallo–cyanide complexes and thiocyanate can be determined by ion-interaction chromatography with UV detection [4–6]. However, cyanide and cyanate are both unretained on such a chromatographic system and are also UV transparent. Therefore, in the case of cyanide, pre- or post-column derivatisation techniques have been used to facilitate detection [5,6]. There are no such reactions suitable for the analogous pre- or post-column derivatisation of

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cyanate which are compatible with the above system. Several methods describing the separation and determination of cyanate have been published. Silica based ion-exchangers [7,8], anion-exchange resins [9,10] and ion-interaction reversed-phase liquid chromatography [11–13], have all been used for the separation of cyanate. Each of these studies has found that cyanate is weakly retained, being eluted shortly after chloride.

Only one of the above papers has described a method for the analysis of cyanate and other anions which has been developed specifically for the gold processing industry [13]. Here, ion-interaction chromatography was used with a reversed-phase column permanently coated with cetylpyridinium chloride, with 1,3,5-benzenetricarboxylic acid–Tris buffer being employed for the mobile phase. However, cyanate and chloride were unresolved and therefore the method was not suitable for the determination of cyanate in samples containing large excesses of chloride. One of the best reported separations of cyanate and chloride was obtained on a Hamilton PRP X100 column with a 4-amino-2-hydroxybenzoic acid (2 m*M*) eluent [14]. However, the instability of aqueous solutions of 4-amino-2-hydroxybenzoic acid restricted the applicability of this method [15]. In all of the above methods, either suppressed conductivity [9,10] or indirect UV detection [7,8,11,13,14] were used for detection of cyanate.

Indirect UV detection was used in the present study since it enabled the same detector to be applied to both this analysis and to the separate analysis of metallo–cyanide complexes using the ion-interaction method mentioned previously. This detection approach necessitated the use of an aromatic carboxylic acid for the eluent in order to provide both a weak eluent and one containing a strong UV chromophore [16].

2. Experimental

2.1. Instrumentation

The instrumentation used consisted of two HPLC pumps, a Waters M-510 pump for delivering the mobile phase and a Waters M-600E gradient pump for backflushing the guard column (Waters, Milford, MA, USA). Samples and standards were injected with a Waters M-717 WISP HPLC autosampler fitted with either a standard 250-μl or a micro 25-μl syringe. Injection volumes for the automated, on-line removal of the metallo–cyanide complexes were between 1 and 10 μl. A Waters 6-port, 2-way Automated Switching Valve unit was used for switching the flow direction on the guard column. A Waters M-486 variable-wavelength detector set at 355 nm was used for indirect UV detection. Instrument control and data handling were performed with a Waters Millennium data system. A Waters high capacity IC-Pak A (150 mm×4.6 mm I.D.) analytical column and a Waters guard column fitted with Waters IC-Pak A Guard-Pak inserts were used.

Supelclean LC-SAX (Supelco, Bellefonte, PA, USA) solid-phase extraction (SPE) cartridges were used for the manual removal of metallo–cyanide complexes from samples prior to the IC analysis. These SPE cartridges contained 500 mg of a quaternary amine strong base anion-exchanger (SAX) in the chloride form. Prior to use, the SPE cartridges were conditioned with methanol (2 ml) followed by water (2 ml) and then flushed with 5 aliquots (2 ml) of I5 m*M* Na_2S0_4. Solutions were manually pushed through the SPE cartridge with a syringe at a flow-rate of approximately 2 ml min^{-1}.

2.2. Reagents

Anthranilic acid (Ajax, Auburn, Australia), benzoic acid (May and Baker, Dagenham, UK), *o*-phthalic acid (BDH, Port Fairy, Australia) and salicylic acid (Aldrich, Castle Hill, Australia), were used as supplied. These carboxylic acids were all of analytical reagent-grade quality. Eluents were prepared by dissolving the carboxylic acid in a dilute NaOH solution. The eluent used for most of this work was a 10 m*M* solution of anthranilic acid (pH 6.7). All the eluents were filtered (0.45 μm) and degassed prior to use. The anthranilic acid eluents were prepared freshly each day.

Sodium cyanate (Aldrich) was used to prepare the cyanate standards. Standardisation was carried out using the Kjeldahl nitrogen method. The purity of the sodium cyanate was found to be 96.4%. The other standards and reagents were prepared from analytical reagent grade salts. The cyanate standards

were prepared in 10 m*M* NaOH solution and stored in a refrigerator. Deionised water obtained from a Milli-RO water purification system (Millipore, MA, USA) was used for preparing all solutions.

2.3. Samples

Samples were obtained from various cyanidation plants at the Telfer gold mine, Western Australia. Most of the samples were filtered on collection and the clear filtrates were analysed without further treatment. The samples from the pyrite leach plant contained very fine suspensions and were further filtered with disposable 0.45-μm Millex filters (Millipore).

3. Results and discussion

3.1. Selection of separation conditions

The process samples for which the methods described in this paper were developed contained large concentrations of cyanide, metallo–cyanide complexes [especially Cu(I)–cyanide complexes], thiocyanate, chloride and sulfate. The typical range of chloride and sulphate concentrations in these samples were 43–86 m*M* and 16–32 m*M*, respectively. For this reason, a high capacity anion-exchange analytical column was employed to reduce overloading effects due to chloride and sulfate.

Metallo–cyanide complexes are known to have a very strong affinity for anion-exchange resins [17,18]. Consequently, these complexes are very strongly retained on the above anion-exchange columns when a weak eluent is used. This can result in reduced column efficiency and a drifting baseline if the complexes are not flushed off the column after each injection. To avoid this, the metallo–cyanide complexes were removed from the samples prior to injection onto the analytical column with one of two procedures described later in Sections 3.2 and 3.3.

A preliminary investigation examining the separation of 56 m*M* chloride, 0.6 m*M* cyanate and 10 m*M* sulfate was undertaken using eluents prepared from four aromatic carboxylic acids. The four acids investigated were anthranilic, benzoic, *o*-phthalic and salicylic acids. The best separation of cyanate, chloride and sulfate was achieved with an anthranilic acid eluent, which is consistent with results from a previous comparative study of substituted aromatic monocarboxylic acids in which it was noted that anthranilic acid was a particularly weak eluent [19]. As a result of this investigation, all further work was conducted with an anthranilic acid eluent.

The eluent pH was important for several reasons. The most important consideration was to ensure that the eluent pH was greater than the pK_a value of the carboxylic acid in the eluent so that the carboxylate group could act as an eluting anion. It was also necessary to have an eluent pH between 4 and 7 so that cyanate would be retained whilst cyanide was unretained and eluted as HCN. The pK_a values of HOCN and HCN are 3.7 and 9.2, respectively [15]. The carboxylate and amino groups in anthranilic acid have pK_a values of 2.14 and 4.92, respectively [20], but although these pK_a values indicate that the carboxylate group is fully dissociated at pH 5, no peaks were observed in a 10 m*M* eluent at pH 4.9. When the eluent pH was increased to 6.0, a large system peak was observed at a retention time of 20 min. When the eluent pH was then further increased to 6.7, an excellent separation was observed, without any system peak. There was also a considerable improvement in sensitivity when the eluent pH was increased from 6.0 to 6.7. The retention times obtained with this final eluent for some common anions and cyanate are shown in Table 1. It should be noted that nitrate and sulfate were not completely resolved when large sulfate concentrations were present in the sample. However, this was not considered to be a problem as there were generally only negligible amounts of nitrate in the samples analysed. The presence of nitrate was indicated by a fronted sulfate peak.

Table 1
Retention times for some common anions and cyanate

Anion	t_R (min)
Carbonate	3.60
Chloride	5.08
Cyanate	6.59
Nitrate	8.88
Sulphate	9.53

Separation on a Waters high capacity IC-Pak A column with an eluent composed of 10 m*M* anthranilic acid (pH 6.7).

Over a 12-h period a gradual darkening of the eluent was observed, and over 24 h, the eluent pH had increased slightly. These changes were attributed to the oxidation of the amino group in anthranilic acid. Due to these changes, a fresh eluent needed to be prepared each day. It was also noticed that there was a gradual deterioration of the column performance. This deterioration was attributed to oxidation product(s) of anthranilic acid blocking exchange sites, or to the presence of small residual amounts of the metallo–cyanide complexes remaining on the column after sample analysis, resulting in the gradual loss of exchange sites within the column. There was some recovery in the column performance after the column was flushed with 10 m*M* HNO_3. However, even with periodic HNO_3 flushes, the column performance was sufficiently reduced after six weeks of operation to render the column unusable.

The analytical parameters for the determination of cyanate under the optimal eluent conditions were studied. Calibration linearity was determined for cyanate and the calibration plot was linear at least over the range 10–120 nmol injected onto the analytical column. For an injection volume of 10 μl this corresponds to the concentration range 1–12 m*M*. The two major anions present in the samples were chloride and sulfate. Consequently, the effect of large concentrations of these two anions on cyanate was examined. The cyanate peak area was the same for a 0.57 m*M* cyanate standard and another standard containing the same cyanate concentration in the presence of a 100-fold excess of both chloride and sulfate. From this experiment, it was concluded that the optimal separation conditions could tolerate at least a 100-fold excess of both chloride and sulfate. The detection limit was determined at the point where the cyanate peak height was three times the average baseline noise. The observed detection limit for a 50 μl injection volume was 9.5 μ*M*. This is equivalent to an absolute detection limit of 0.48 nmol.

3.2. Removal of metallo–cyanide complexes by off-line SPE

The retention of the Cu(I)–cyanide complexes on a SPE cartridge containing 500 mg SAX resin was examined by conditioning the cartridge with 56 m*M* NaCl and then flushing through the cartridge successive 2.0 ml portions of a sample containing 3.7 m*M* Cu(I)–cyanide complexes in 50 m*M* NaCl. The effluent from the cartridge was collected after each sample portion and analysed for copper using atomic absorption spectroscopy (AAS). The results, shown in Table 2, demonstrated that at least 6 ml of the sample [corresponding to 22 μmol of the Cu(I)–cyanide complex] could be loaded onto the SAX sorbent before breakthrough occurred. Previous studies have suggested that the copper(I) would be retained on the cartridge predominantly as the $Cu(CN)_2^-$ complex [21].

Since cyanate from the sample would also be retained on the cartridge and would be required to be eluted before analysis, it was necessary to choose an eluting anion which did not interfere in the cyanate analysis. It was also necessary that cyanate be stripped from the cartridge in a small volume to prevent sample dilution and that no Cu(I)–cyanide complex be eluted with the cyanate fraction. Experiments were conducted with carbonate, chloride or sulfate as the anion in the stripping eluent, with best results (98% recovery of cyanate) being obtained using 15 m*M* Na_2SO_4. When 2.2 ml of 15 m*M* Na_2SO_4 was used as the stripping eluent after loading 200, 300 and 400 μl volumes of a sample containing Cu(I)–cyanide complexes (36.7 m*M*),

Table 2
Breakthrough study of Cu(I)–cyanide complexes on a SPE cartridge containing 500 mg of a SAX sorbent

Sample volume (ml)	[Cu] in effluent (n*M*)	Sample volume (ml)	[Cu] in effluent
Blank	<15	8.0	47 n*M*
2.0	<15	10.0	110 n*M*
4.0	<15	12.0	19 μ*M*
6.0	<15	14.0	1.3 m*M*

The SPE cartridge was conditioned prior to use with a NaCl solution (56 m*M*). The sample contained Cu(I)–cyanide complexes (3.67 m*M*) in a NaCl solution (50 m*M*). The blank was a NaCl solution (56 m*M*).

copper was only detected in the effluent from the SPE cartridge when 400 μl of the sample was used. The injection volume of the SPE effluent onto the analytical column was also investigated. It was observed that a 50 μl injection volume enabled the cyanate peak and the large sulfate peak (from the stripping eluent) to be baseline resolved, as shown in Fig. 1. Increasing the injection volume to 100 μl caused the sulfate peak to merge with the cyanate peak.

From the above investigations, the following method was adopted for the SPE removal of Cu(I)–cyanide complexes. The SAX sorbent in the SPE cartridge was conditioned as described in the Section 2.1, after which 200 μl of sample was slowly loaded onto the SAX sorbent, followed by 2.2 ml of 15 m*M* Na_2SO_4. The entire effluent from the SPE cartridge was collected and placed directly into an autosampler vial, from which 50 μl was injected onto the analytical column for analysis.

Two samples were prepared for analysis using this method with each sample preparation being performed in duplicate. It was observed that there was up to a 9% variation between the results from the duplicate preparations. This variation was attributed primarily to the SPE step since the variation between duplicate injections of the same sample was approximately 1%. The variation in the SPE method was further investigated. Thirteen samples were prepared by the above method and the mass of eluate collected from each SPE cartridge in the auto-sampler vials was recorded. The mass of eluate collected in the vials varied from 2.250–2.435 g with a mean mass of 2.369 g and a standard deviation of 0.057 g. These results indicated that dilution of each eluate to a constant mass in the autosampler vial would considerably improve the reproducibility of this method. However, this dilution step would have increased the sample preparation time and thus this approach was not pursued. This decision was taken as a method was required for the analysis of a large numbers of samples. However, it should be noted that the SPE method with a dilution step would be useful for the analysis of a small number of samples due to the considerable additional capital costs involved in the following on-line method for the removal the Cu(I)–cyanide complexes.

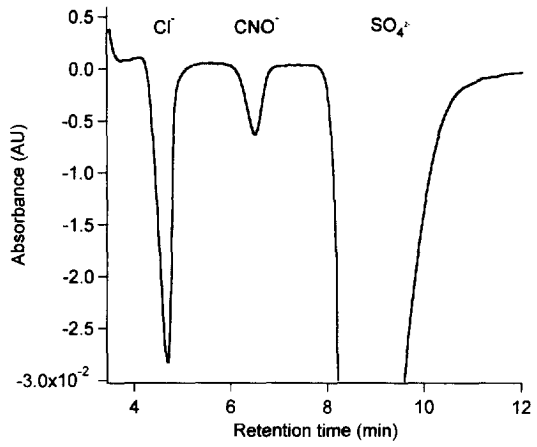

Fig. 1. Chromatogram of a cupriferous leach sample after the manual off-line removal of metallo–cyanide complexes with a SPE cartridge containing a strong anion exchanger. The CNO^- was eluted from the SPE cartridge with 2.2 ml Na_2SO_4 (15 m*M*).

3.3. Removal of metallo–cyanide complexes by an on-line method

As a result of the difficulties encountered with the off-line SPE method, an on-line method utilising a 6-port, 2-way, column switching valve and a guard column was developed. In this approach, the metallo–cyanide complexes were retained on the guard column, while cyanate was eluted off the guard column directly onto the analytical column. By operation of the column switching valve, it was then possible to backflush the guard column and remove the adsorbed metallo–cyanide complexes with a second pump as shown in Fig. 2.

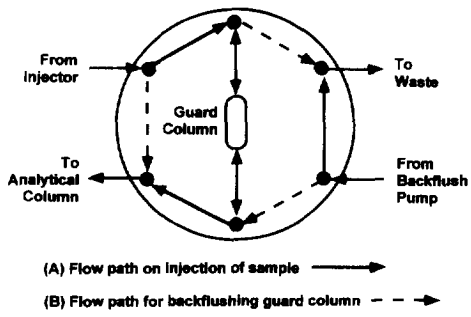

Fig. 2. Configuration of a column switching valve and guard column for the on-line removal of metallo–cyanide complexes. The complexes are backflushed off the guard column with the anthranilic acid eluent by a second pump.

The first step in developing this method was to determine the residence times of the cyanate and Cu(I)–cyanide complexes on the guard column using an anthranilic acid eluent. The elution of the Cu(I)–cyanide complexes was studied by injecting a sample onto the guard column, passing the anthranilic acid eluent through the guard column and collecting aliquots every 30 s. The Cu concentration was then determined in these aliquots, after dilution, using AAS. When 5 μl of a sample containing Cu(I)–cyanide complexes (57.4 m*M*) was injected onto the guard column, 91% of the total Cu injected was recovered in 3 min. No Cu was detected in the effluent from the guard column in the first 30 s, 1.7% of the injected Cu was detected in the subsequent 30 s and 72% of the Cu was eluted off the guard column in the following minute. When the guard column was dismantled, it was obvious that a noticeable darkening of the packing material in the insert had occurred with the most pronounced darkening on the front of the insert. This was attributed to the Cu which was not eluted from the guard column. When a dilute HNO_3 (7 m*M*) solution was used to backflush the guard column, most of the darkening disappeared indicating that most of the Cu had been removed.

The guard and analytical columns were then connected to the column switching valve using the configuration shown in Fig. 2. The time required to completely elute HCO_3^-, Cl^-, CNO^- and SO_4^{2-} off the guard column was then studied. This was achieved by turning the switching valve from the injection position to the backflush position, at the various switching times shown in Fig. 3. These results show that the four anions were completely eluted off the guard column in 30 s. Consequently the switching valve was set to turn 30 s after injection.

Regeneration of the guard column was then addressed. Use of HNO_3 solution (10 m*M*) to backflush the guard column and thereby remove the bound Cu(I)–cyanide complexes was unsuccessful as only 93% of the Cu was removed from the guard column in 28 min, with most (71%) of the Cu being removed in the first 4.7 min. However, backflushing of the guard column with the anthranilic acid resulted in complete elution of the Cu in 6 min, presumably due to the ability of anthranilic acid with

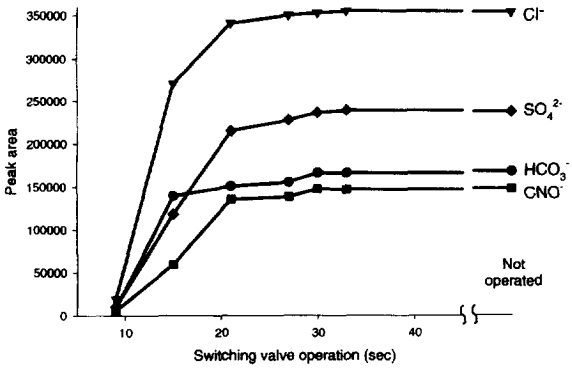

Fig. 3. Effect of switching valve operation time on peak areas (arbitrary units) of four anions following injection of sample. The switching valve is turned after the injection of sample to enable backflush of the guard column. The final point for each anion shows the peak areas obtained when the switching valve was not turned following injection of sample. This comparison shows that these four anions were completely eluted off the guard column in 30 s.

respect to complexation of Cu(II) [22]. The regeneration cycle consisted of ramping the flow-rate of the backflush pump from 0–1.5 ml min^{-1} over a 1.5 min period after the switching valve was turned. This flow-rate was then maintained for 3 min, after which the flow was reduced progressively to zero over an additional 1.5 min. These slow changes in flow-rate were used to minimise damage to the guard column. The switching valve was turned back to the injection position just prior to the commencement of a new analysis.

The level of sample dilution to be used was investigated. In order to prevent overloading the guard column with Cu(I)–cyanide complexes and overloading the analytical column with chloride and sulfate, samples were normally diluted four-fold with deionised water in 4.5 ml autosampler vials and 10 μl injection volumes were used. Whilst this approach was used satisfactorily for over 200 samples, the method was adapted to the injection of undiluted samples by replacing the standard autosampler syringe with a 25-μl microsyringe and reducing the injection volume to 2 μl. The precision for the cyanate peak area was 1.4% R.S.D. for 5 replicate 2 μl injections of a sample.

3.4. Analysis of samples

Prior to the analysis of samples, the reaction between Cu(II) and cyanide was used to test the on-line removal of Cu(I)–cyanide complexes and subsequent IC analysis for cyanate. In this reaction, Cu(II) is reduced and complexed by cyanide to form Cu(I)–cyanide complexes, while the oxidised cyanide forms cyanogen which then undergoes rapid hydrolysis in alkaline solution to form cyanate as shown below [23].

$$Cu^{2+} + 2CN^- \rightarrow CuCN + 1/2(CN)_2 \quad (1)$$

$$(CN)_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \quad (2)$$

In this experiment, solid $CuCl_2$ (2.5 mmol) was dissolved in an alkaline solution containing excess NaCN (12.5 mmol). Dissolution occurred in less than 1 min to form a clear solution, which was then diluted to 250.0 ml and injected immediately after dilution (5 min after the $CuCl_2$ was added to the NaCN solution) and then at two successive 9-min intervals. The cyanate concentration in these injections was found using the on-line sample treatment method to be 5.00, 4.97 and 4.95 m*M* respectively (expected cyanate concentration was 5.0 m*M*), thereby establishing the validity of the proposed approach for the determination of cyanate in the presence of Cu(I)–cyanide complexes.

Samples were collected from two cyanide leaching operations at the Telfer gold mine. The first operation involved the cyanidation of untreated cupriferous gold ores, whilst the second involved the cyanidation of material obtained from a pyrite flotation process. In the latter process various sulfurous flotation agents are added during the initial treatment of pyritic gold ores in order to remove metal sulfide concentrates, after which the remaining ore slurry is fed into a cyanide leaching tank. The cyanide leach samples obtained from the cupriferous and pyrite leach operations contained up to 63 m*M* and 150 m*M* of Cu(I)–cyanide complexes, respectively. In addition, the pyrite leach samples contained up to 93 m*M* thiocyanate and 7 m*M* $Fe(CN)_6^{4-}$. The samples obtained from the pyrite leach operation were diluted by a factor of 10 with deionised water prior to analysis due to the very large concentrations of Cu(I)–cyanide complexes. Typical chromatograms of samples from both leaching operations are shown in Figs. 4 and 5. The major anions identified in these chromatograms were carbonate, chloride, sulfate and thiosulfate (present in the pyrite leach samples as one of the flotation reagents). Cyanate concentrations were generally in the range 2.4–10 m*M* for the cupriferous leach samples and up to 45 m*M* in the

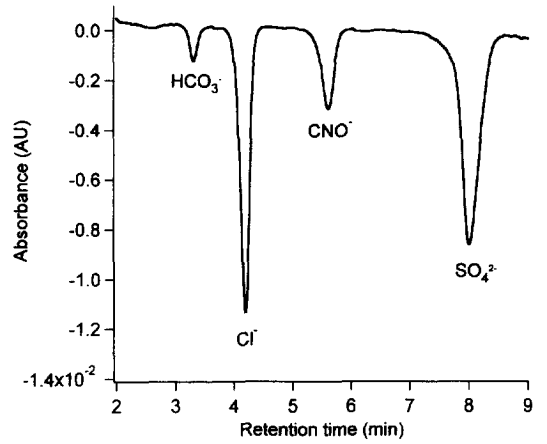

Fig. 4. Chromatogram of a cupriferous leach sample after the on-line removal of the metallo–cyanide complexes.

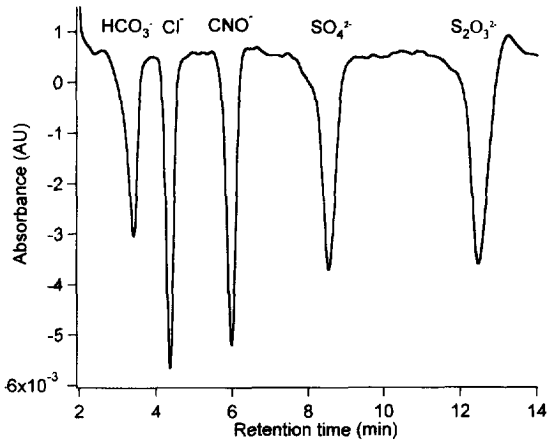

Fig. 5. Chromatogram of a pyrite leach sample after the on-line removal of the metallo–cyanide complexes.

pyrite leach samples, indicating considerable cyanide oxidation in these latter samples. Since no thiocyanate was observed in chromatograms of the pyrite leach samples, it was assumed that this strongly retained anion was also trapped on the guard column along with the metallo–cyanide complexes.

3.5. Comparison of IC and Kjeldahl methods for cyanate analysis

Some samples obtained from the cyanidation of high grade cupriferous gold ores containing high concentrations (78–95 m*M*) of the Cu(I)–cyanide complexes were analysed for cyanate using a standard method [24]. This method involves the Kjeldahl digestion of the sample, followed by ammonia analysis.

A comparison of the results obtained by the IC and Kjeldahl methods is shown in Table 3, which indicates that a large discrepancy exists between the two methods, with the IC method reporting a considerably lower cyanate concentration. This interference was further investigated using Cu(I)–cyanide standards (prepared by mixing CuCN and cyanide) containing Cu concentrations between 16 and 470 m*M* and a CN:Cu mole ratio of 3, as shown in Table 4. The results of this study showed that significant levels of cyanate, were recorded by the Kjeldahl method in the presence of Cu(I)–cyanide complexes, despite the fact that no cyanate was detected in these Cu(I)–cyanide standards using the IC method. The source of error in the Kjeldahl method is not known but may be due to the production of cyanate during the acid hydrolysis step of the Kjeldahl analysis during which copper(II) is formed and then reacts in a manner similar to that depicted in Eqs. (1,2). The same effects of Cu(I)–cyanide complexes on the Kjeldahl analysis were observed at CN:Cu mole ratios of 4 and 5, which reflect the range of typical values found during the cyanidation of cupriferous ores.

Table 3
Comparison of cyanate analyses using the Kjeldahl and IC methods

Sample	[OCN^-] (m*M*)	
	Kjeldahl method	IC method
1	5.00	2.69
2	5.59	3.83
3	8.09	5.66
4	12.6	7.00
5	10.0	6.12

The samples contained large concentrations (78–95 m*M*) of Cu(I)–cyanide complexes.

Table 4
Cyanate analysis using the Kjeldahl hydrolysis method of standards of various Cu(I)–cyanide complexes

[CN] (*M*)	[Cu] (*M*)	CN:Cu mole ratio	[CNO^-] (m*M*)
0.192	0.000	–	0.14
0.047	0.016	3.0	1.33
0.165	0.055	3.0	7.81
0.236	0.079	3.0	16.54
0.473	0.157	3.0	22.94
0.707	0.236	3.0	30.53
1.414	0.472	3.0	26.13

Note that the formation of cyanate becomes significant at higher Cu concentrations, irrespective of the CN:Cu mole ratio.

The above results show the unreliability of the Kjeldahl method for the determination of cyanate in the presence of significant levels of Cu(I)–cyanide complexes and suggest that the IC method offers significant advantages for the analysis of such samples.

4. Conclusions

A new ion chromatographic method for the analysis of cyanate in gold processing samples has been developed, specifically for samples containing large concentrations of metallo–cyanide complexes. The most important aspect of this method is the incorporation of the sample clean-up step for the removal of metallo–cyanide complexes prior to injection of the sample onto the analytical anion-exchange column.

Two methods for the removal of metallo–cyanide complexes were developed. The simplest method involves the use of SPE cartridges containing a strong anion-exchanger and can be used with a standard HPLC instrument. The second method enables the on-line clean-up by utilising a column switching valve and a second pump. This on-line method was developed for the analysis of large numbers of samples on an automated basis.

When the IC analysis was compared to the

standard Kjeldahl method for the analysis of cyanate, it was observed that in the latter technique, a significant interference occurred when a large concentration of complexed Cu(I)–cyanide was present.

Acknowledgments

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