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Ion chromatographic determination of cyanate in saline gold processing samples

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Abstract

An ion chromatographic method was developed for the determination of cyanate (CNO^-) in saline gold processing samples. The method is based on the use of a very weak-eluting buffer (5 m*M* sodium borate) and a Dionex AS4A-SC anion-exchange column. This weak-eluting buffer facilitates the wide chromatographic separation of chloride (Cl^-) from CNO^-. After CNO^- has been eluted, the switch to 1.8 m*M* Na_2CO_3–1.7 m*M* $NaHCO_3$ buffer allows the fast elution of other major inorganic and organic anions. Validation of this method, including identification of interferences, has shown that this method is reliable, accurate, sensitive (detection limit, 0.1 mg/l CNO^-) and reproducible.

Keywords: Saline gold processing samples; Cyanate

1. Introduction

Cyanate (CNO^-), produced from the oxidation of cyanide is of interest to the gold processing industry both; during the gold cyanidation process and in their waste waters for environmental reasons. During the gold cyanidation process, oxidation of cyanide to CNO^- is one way in which the expensive reagent cyanide is lost and thus more sodium cyanide is required for the leaching of gold from the ore material. In industrial cyanide leach waste, CNO^- itself has low toxicity. However, on acidification it decomposes to ammonia. Molecular ammonia and metal–ammonia complexes are toxic to aquatic life [1].

Prior to the development of an ion chromatographic method for the analysis of cyanate, our laboratory used a colorimetric method. The colorimetric method [1] involved acidic hydrolysis of cyanate by heating at low pH to form ammonia. The ammonia content before and after hydrolysis of cyanate was measured colorimetrically by using phenol and hypochlorite to form the indophenol blue complex. This colorimetric method was shown to be unreliable for some gold processing samples and for samples containing low levels of CNO^- in the presence of high concentrations of metals or ammonia. The procedure for this method was long, time consuming and the outcome of results was heavily operator dependent. It was decided to develop an ion chromatographic method for its ease of operation and the elimination of ''operator dependency'' by its automation.

There are few methods reported in the literature for the analysis of CNO^- [2–12] and only two of

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these methods have been developed for the gold processing industry [3,5]. Various authors [3,7–12] reported ion chromatographic techniques for CNO^- analysis of samples containing low Cl^- levels. These methods were not suitable for saline samples. Fagan et al. [5] reported an ion chromatographic method which was suitable for samples with Cl^- levels up to 100-fold higher than the CNO^- concentration and a detection limit of 0.39 mg/l for CNO^- (i.e., up to 40 mg/l Cl^-). However they experienced rapid column deterioration which would make this technique very expensive for routine CNO^- analyses.

In this paper we report an ion chromatographic method for the quantitative analysis of CNO^- which is sensitive, robust, with no rapid column deterioration and suitable for saline gold processing samples.

2. Experimental

2.1. Instrumentation

The instrumentation used consisted of a Waters 600E pump and delivery system controller, a Waters 700 Satellite WISP autosampler, a Waters 431 conductivity detector, a Dionex AS4A-SC (4 mm) column, a Dionex AG4A-SC (4 mm) guard column and a Dionex anion membrane suppressor AMMS-II with 0.0125 *M* H_2SO_4 suppression. Data collection and processing were carried using Data Acquisition, Plotting and Analysis (DAPA) software.

2.2. Reagents and materials

Potassium cyanate, sodium borate, sodium carbonate, potassium thiocyanate and sodium hydrogencarbonate were of analytical-reagent grade. The latter was obtained from Ajax and the rest were obtained from BDH. All standard solutions of cyanate were prepared in 5 m*M* NaOH and stored in a refrigerator. The water used was Milli-Q water obtained from a Millipore Milli-Q water purification system. Helium gas was high-purity grade.

Potassium hexacyanoferrate (II) and (III) [$Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively], potassium dicyanoaurate (I) [$Au(CN)_2^-$], potassium hexacyanocobaltate (III) [$Co(CN)_6^{3-}$], potassium tetracyanonickelate (II) [$Ni(CN)_4^{2-}$], potassium dicyanosilver (I) [$Ag(CN)_2^-$] and potassium hexacyanochromate (III) [$Cr(CN)_6^{3-}$] were purchased from Strem Chemicals as pure compounds. Potassium tetracyanocuprate (I) [$Cu(CN)_4^{3-}$] was synthesised using a previously published procedure [13]. Standard solutions of thiocyanate and metal cyanide complexes were prepared with Milli-Q water.

Sodium borate (5 m*M*) was prepared by dissolving 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ in 5000 ml water. The water was previously degassed by bubbling helium gas through it for 10 min. The solution was filtered through a 0.45-μm membrane filter.

For carbicarb concentrate 19.1 g Na_2CO_3 and 14.3 g $NaHCO_3$ were dissolved in 1000 ml water. The solution was filtered through a 0.45-μm membrane filter.

The 1.8 m*M* Na_2CO_3–1.7 m*M* $NaHCO_3$ buffer was prepared by diluting 50 ml carbicarb concentrate to 5000 ml with water. The solution was degassed by bubbling helium gas through it for 10 min.

2.3. Procedure

The initial mobile phase for analysis of CNO^- was 5 m*M* sodium borate buffer. At 15 min (after elution of CNO^-), the mobile phase was switched to 1.8 m*M* Na_2CO_3–1.7 m*M* $NaHCO_3$ to elute the rest of the sample components. At 30 min, the mobile phase was switched back to 5 m*M* sodium borate to equilibrate the system before injection of the next sample.

All chromatographic separations were carried out at ambient temperature, using a mobile phase flow-rate of 2.0 ml/min and a 50 μl sample injection volume.

3. Results and discussion

The 5 m*M* sodium borate is a very weak-eluting buffer for anions, which facilitates the wide separation of Cl^- from CNO^- (Fig. 1). After CNO^- has been eluted, the switch to 1.8 m*M* Na_2CO_3–1.7 m*M* $NaHCO_3$ buffer allows the fast elution of other major inorganic anions such as Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and organic anions such as oxalate and phthalate (Table 1) which are not determined. This

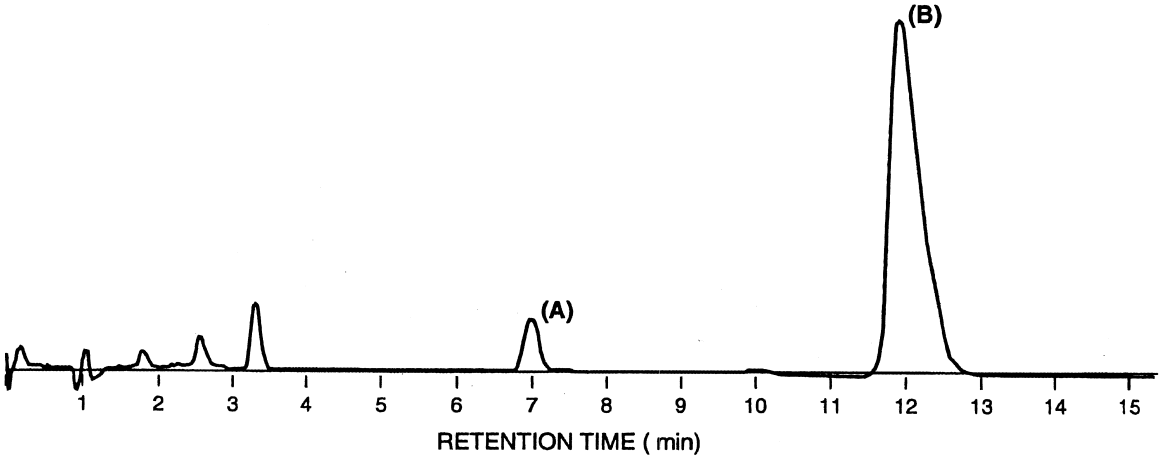

Fig. 1. Chromatogram of (A) 0.1 mg/l Cl^- and (B) 5 mg/l CNO^- standard in 5 m*M* NaOH.

Table 1
Retention times (t_R) for some common anions and cyanate

Anion	t_R (min)
Fluoride	2.3
Acetate	2.6
Formate	3.3
Chloride	7.2
Cyanate	11.1
Nitrite	>15
Bromide	>15
Nitrate	>15
Phosphate	>15
Sulphate	>15
Oxalate	>15

faster eluting buffer flushes the column from the remaining components of the sample. The column is then re-conditioned with 5 m*M* sodium borate buffer, to be ready for the next sample. No shift in baseline was observed after analysis of each sample.

Precision data are shown in Table 2. Recovery studies involved the spiking of two gold processing samples. The recoveries were 88% and 94% at CNO^- concentrations of 2.0 and 6.1 mg/l, respectively. CNO^- response was found to be linear up to 10 mg/l. The detection limit was 0.1 mg/l, based on a signal-to-noise ratio of 4.

Table 2
Precision of CNO^- analysis in gold processing samples (n=5)

Sample	Mean±SD (mg/l)	RSD (%)
A	122±4.9	4.0
B	20±1.1[a]	5.5
C	724±27	3.7
D	1.41±0.03	2.1
E	0.32±0.04	12

[a] n=4.

A new column was used for the routine analysis of CNO^- in gold processing solutions for a period of six months with no obvious deterioration of the column.

3.1. Salinity studies

The wide separation between Cl^- from CNO^- facilitates analysis of saline samples (Fig. 2). The detection limit of CNO^- was found to be dependent on the Cl^- concentration. At levels less than 500 mg/l Cl^- (~1000 mg/l salinity) the limit of detection is 0.1 mg/l. Samples with Cl^- levels higher than 500 mg/l need to be diluted to eliminate Cl^- interference. Thus, at levels of 50 000 mg/l Cl^- (~100 000 mg/l salinity) the limit of detection is 10 mg/l.

A salinity trial was carried out to test robustness of the method with respect to salinity levels. A batch of substitute ocean water (OW) was prepared in the laboratory following ASTM guidelines [14]. A batch of dilute ocean water (DOW) was prepared by diluting 50 ml of OW to 5000 ml with Milli-Q water. A batch of saturated ocean water (SOW) was prepared by weighing constituents four-fold higher

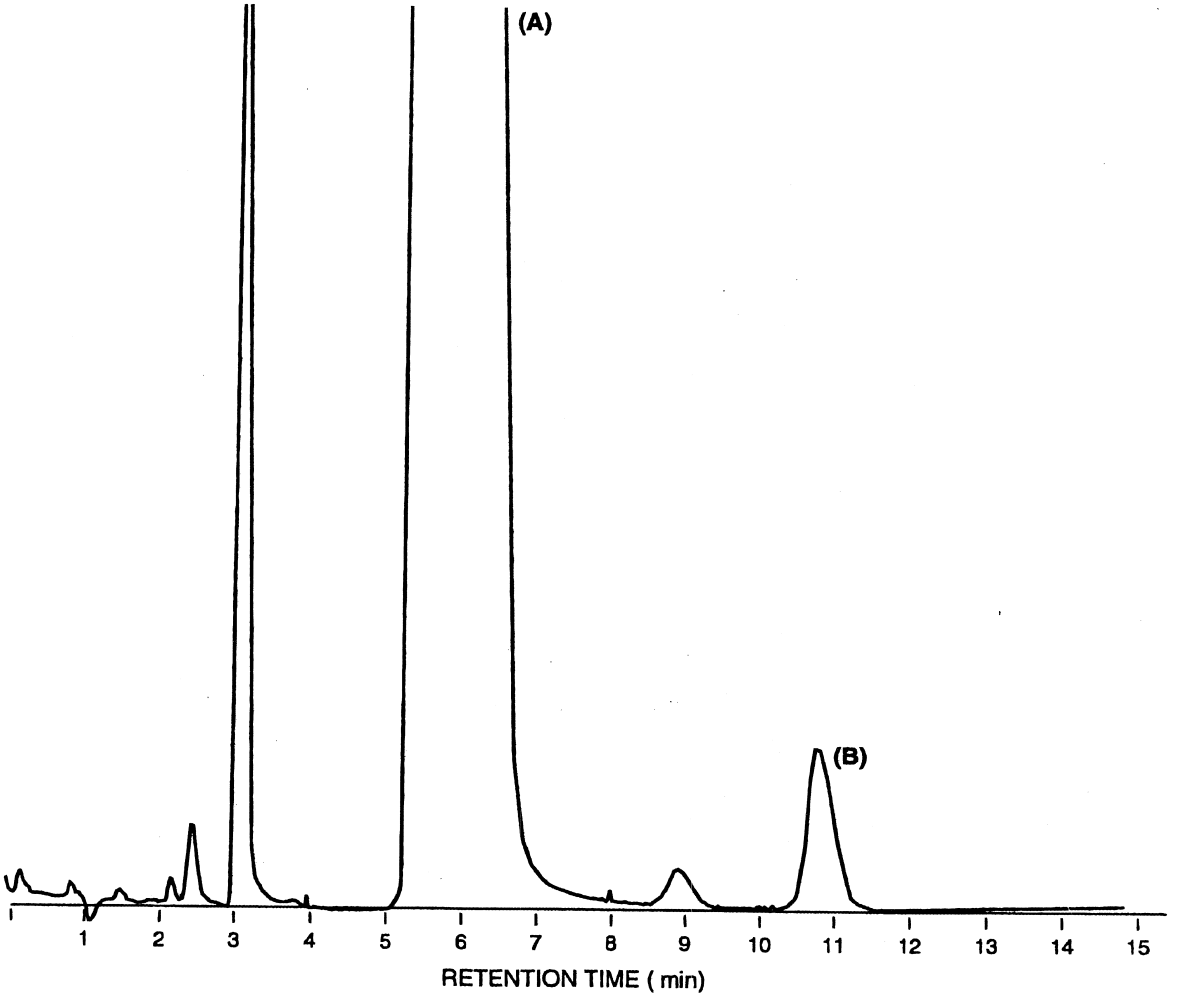

Fig. 2. Chromatogram of a gold processing sample containing (A) 1300 mg/l Cl^- and (B) 20 mg/l CNO^-. The sample was diluted 1:10 with water prior to analysis.

than those of OW. These solutions were analysed for Cl^-, pH and salinity levels.

Standard solutions of 5 mg/l CNO^- were prepared in OW, DOW and SOW. These standards and their respective blanks were analysed by this method. The results (Table 3) showed that at Cl^- and salinity concentrations of 180 and 370 mg/l, respectively, the CNO^- detection limit was 0.1 mg/l. At Cl^- and salinity levels of 15 000–71 000 and 30 000–107 000 mg/l, respectively, the samples needed to be diluted and the CNO^- detection limit increased in proportion to the dilution factor. Gold processing samples having salinity levels of 100 000 mg/l had a detection limit of 10 mg/l CNO^-. Samples H, I and M are real gold processing samples. Sample J is sample OW spiked with CNO^- (final CNO^- concentration, 15 mg/l). Samples K and L are sample SOW spiked with CNO^- (final CNO^- concentrations, 15 and 50 mg/l, respectively). Samples H to M demonstrate how the salinity and specifically chloride concentration affect the CNO^- detection limit. Samples J, K and L confirm that at salinity

Table 3
Detection of CNO^- at different Cl^- and salinity levels

Sample	Cl^- concentration (mg/l)	Salinity[a] (mg/l)	pH	CNO^- concentration (mg/l)
DOW	180	370	7.3	<0.1
OW	15 000	30 000	8.3	<10
SOW	71 000	107 000	7.4	<10
Sample H	2100	5000	7.6	<1
Sample I	2500	5200	8.8	47
Sample J	15 000	30 000	8.3	15
Sample K	71 000	107 000	7.4	11
Sample L	71 000	107 000	7.4	41
Sample M	97 000	100 000	9.4	16

[a] Salinity calculated from conductivity values.

levels of 30 000 to 107 000 mg/l, CNO^- can be detected and quantified if it is above 10 mg/l (CNO^- detection limit, 10 mg/l).

3.2. Interferences

The possible interference of individual metal cyanide complexes was examined as well as possible interference from other compounds which are commonly found in tailing solutions from gold processing plants (Table 4). It was found that ammonia, cyanide (CN^-), thiocyanate (SCN^-), thiosulphate ($S_2O_3^{2-}$) and metal cyanide complexes of Co, Ni, Au, Cu and Ag did not interfere with the CNO^- analysis.

Table 4
Study of possible interference of metal cyanide complexes and other compounds on the CNO^- method

Analyte	Analyte concentration (mg/l)	CNO^- concentration (mg/l)
$S_2O_3^{2-}$	10	<0.1
CN^-	1, 10 and 100	<0.1
SCN^-	100	<0.1
$Co(CN)_6^{3-}$	100 as metal	<0.1
$Ni(CN)_4^{2-}$	100 as metal	<0.1
$Au(CN)_2^-$	100 as metal	<0.1
$Ag(CN)_2^-$	100 as metal	<0.1
$Fe(CN)_6^{4-}$	100 as metal	0.10
$Fe(CN)_6^{3-}$	100 as metal	0.50
$Cu(CN)_4^{3-}$	100 as metal	<0.1
NH_3	2000	<0.1

However, 100 mg/l iron levels of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ were detected as a CNO^- response of 0.10 and 0.50 mg/l, respectively.

4. Conclusion

This method has a detection limit of 0.1 mg/l for cyanate in samples with salinity levels of up to 1000 mg/l. The method is suitable for more saline samples when appropriately diluted before analysis. The cyanate detection limit for real gold processing samples containing 100 000 mg/l salinity is 10 mg/l.

Validation of this ion chromatographic method for analysis of cyanate has shown that this method is reliable, accurate, sensitive and reproducible.

Interference studies showed that this method is suitable for the analysis of samples containing CN^-, SCN^-, thiosulphate ($S_2O_3^{2-}$) and metal cyanide complexes of Co, Ni, Au, Cu, Cr, Fe and Ag. However, Fe(II) and Fe(III) cyanide complexes at levels greater than 100 mg/l (as the metal) may cause minor interferences.

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References

[1] WEF, in: Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995, pp. 18–35.
[2] W.E. Barber, P.W. Carr, J. Chromatogr. 301 (1984) 25.
[3] D.J. Barkley, T.E. Dahms, K.N. Villeneuve, J. Chromatogr. 395 (1987) 631.
[4] T.E. Boothe, A.M. Emran, R.D. Finn, P.J. Kothari, M.M. Vora, J. Chromatogr. 333 (1985) 269.
[5] P. Fagan, B. Paull, P.R. Haddad, R. Dunne, H. Kamar, J. Chromatogr. A 770 (1997) 175.
[6] P. Lundquist, B. Backman-Gullers, B. Kagedal, L. Nilsson, H. Rosling, Anal. Biochem. 211 (1993) 23.
[7] B.R. McCord, Anal. Chim. Acta 288 (1994) 43.
[8] M.C. Mehra, C. Pelletier, Chromatographia 30 (1990) 337.
[9] M. Nonomura, Anal. Chem. 59 (1987) 2073.
[10] M. Nonomura, Metal Finishing: Preparation, Electroplating, Coating 85 (1987) 15.
[11] M. Nonomura, T. Hobo, J. Chromatogr. 465 (1989) 395.
[12] N.E. Skelly, Anal. Chem. 54 (1982) 712.
[13] S.B. Black, R.S. Schulz, Intern. J. Environ. Anal. Chem. 72 (1998) 129.
[14] ASTM, in: Annual Book of ASTM Standards, ASTM, Philadelphia, PA, 1997, p. 404, D1141.