



ELSEVIER

Journal of Chromatography A, 767 (1997) 319–324

JOURNAL OF  
CHROMATOGRAPHY A

## Determination of metal cyanide complexes in gold processing solutions by capillary electrophoresis

Manuel Aguilar, Adriana Farran\*, Vicenç Martí

*Chemical Engineering Department (E.T.S.E.I.B.-U.P.C.), Diagonal 647, 08028 Barcelona, Spain*

Received 9 September 1996; revised 8 November 1996; accepted 4 December 1996

### Abstract

A capillary electrophoresis method to determine metal cyanide complexes and sulphur compounds in gold processing solutions using direct UV absorbance detection has been developed. The method is based on the use of electroosmotic flow modifiers, such as  $C_{17}H_{38}NBr$ , to control the separation and in the on-column concentration of the sample by using the stacking effect to increase the sensitivity. By optimizing the analytical conditions, analysis times of less than 15 min and detection limits of metals in the mid-ppb range have been obtained with good resolution. The quantitation and determination of the metal cyanide complexes  $Au(CN)_2^-$ ,  $Ag(CN)_2^-$ ,  $Cu(CN)_3^{2-}$ ,  $Ni(CN)_4^{2-}$  and  $Fe(CN)_6^{4-}$ ,  $HS^-$  and  $SCN^-$ , present in samples from the leaching of a gold mineral (Minas Gerais, Brazil) and a gold sand (Iténez, Bolivia) by using a sodium cyanide (NaCN) solution (1000 ppm and pH 10.5 adjusted with CaO, as in real processes), has been achieved. Finally, the evolution of the formation within the time of gold cyanide complexes under leaching conditions has been studied by using the analytical method proposed.

**Keywords:** Gold processing solutions; Metal cyanide complexes; Gold cyanide complexes

### 1. Introduction

The main hydrometallurgical process for the recovery of gold from ores is cyanidation, which involves leaching of the crushed ore with an alkaline solution of sodium or potassium cyanide. Cyanidation has displaced obsolete and other less toxic, but uneconomical, processes [1,2].

In the cyanidation process, the crushed and ground mineral is leached with an alkaline solution of sodium cyanide, either by heap, dump, vat or pulp agitation processes, depending on the initial gold concentration. The leaching solution of aurocyanide

is then purified and concentrated using different techniques, normally with solid adsorbents such as activated charcoal or ion-exchange resins. After that, gold is desorbed and purified by electrowinning.

In some cases, in addition to Au(I), the ore may contain Ag(I), base metals (Fe(II), Cu(I), Ni(II), Zn(II), Co(II)) and S, coming from pyrites, carbonates and silicates [2,3]. So, Ag(I) and base metal cyanide complexes,  $HS^-$  and  $SCN^-$ , can be obtained in the leaching process and they will go on to form part of the waste water [2,4].

There are different stages in the process, such as leaching, adsorption and desorption from solid adsorbents, and waste treatment, where analytical control is necessary.

\*Corresponding author.

For many years, the determination of precious and base metals has been accomplished by different analytical methods such as X-ray fluorescence, Atomic Absorption Spectrometry (AAS) and Atomic Emission with Inductively Coupled Plasma (AES–ICP) [2,5–8].

The separation techniques have the advantage, in relation to the mentioned analytical methods, that they allow the simultaneous determination of different metals and their speciation as cyano-complexes. For that reason, some methods either using ion chromatography [9,10] or reversed-phase ion-interaction chromatography [11–14] with conductimetric or spectrophotometric detection have been developed. A new approach is to use capillary electrophoresis (CE), which has proven to be effective in the separation and detection of some metal cyanide complexes [15–18] as well as in the detection of free cyanide [19].

In this paper, a CE method to determine Au(I)-, Ag(I)-, Fe(II)-, Ni(II)-, Cu(I)-cyanide complexes,  $\text{HS}^-$  and  $\text{SCN}^-$ , in gold ore leaching solutions has been developed and the results obtained have been compared with those obtained by previous chemical and mineralogical analyses of solid samples and by the analysis of the same leaching solutions by ICP.

## 2. Experimental

### 2.1. Solutions and reagents

Stock standard solutions of metal cyanide complexes were prepared by dissolution of an accurately weighed amount of the complexes in a 500-ppm solution of alkaline sodium cyanide, followed by dilution, as required.  $\text{NaCN}$  and  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  from Merck (Darmstadt, Germany),  $\text{NaOH}$  and  $\text{CaO}$  from Panreac (Barcelona, Spain),  $\text{KAu}(\text{CN})_2$ ,  $\text{KAg}(\text{CN})_2$  and  $\text{CuCN}$  from Johnson Matthey Chemicals (Karlsruhe, Germany),  $\text{Na}_2\text{Ni}(\text{CN})_4$ , synthesized from  $\text{NiSO}_4$  (Merck) and  $\text{KSCN}$  from Sigma (St. Louis, MO, USA) were used.

Analytical grade  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{NaHCO}_3$  from Merck and  $\text{C}_{17}\text{H}_{38}\text{NBr}$  (TTAB) from Aldrich (Milwaukee, WI, USA) were used to prepare different buffer solutions with pH values between 10.5 and 12.3 for the CE system.

The electrolyte and sample solutions were prepared with water deionized using a Milli-Q system from Millipore, filtered through a 0.45- $\mu\text{m}$  membrane filter from LIDA (Kenosha, WI, USA) and degassed by ultrasonication.

### 2.2. Instrumentation

An ISCO (ISCO, Lincoln, NE, USA) Model 3850 integrated capillary electrophoresis system, equipped with high voltage up to 30 kV and reversible polarity, was used. Samples were introduced by applying a 3.4 kPa vacuum at the detector end of the capillary. Separations were performed at a constant negative voltage with untreated fused-silica capillaries that were 58 cm (32 cm to the detector) and 70 cm (43 cm to the detector) in total length with 0.05 mm I.D. Detection was carried out by on-column measurement of UV absorption (ISCO CV<sup>4</sup>). Data were collected using commercial software (Varian Star Workstation, Sugar Land, TX, USA) on an IBM-compatible 486 computer.

A Philips PW 1404 X-ray fluorescence spectrometer with a rhodium X-ray tube operated at 60 kV and 50 mA, an LiF crystal and scintillation detection were used to determine the major elements of some samples.

An ICP-Spectroflame (SPECTRO, Kleve, Germany) was used to measure the total metal concentrations.

### 2.3. Sample preparation

Two different samples, a gold mineral from Minas Gerais (Brazil) and a gold sand from Iténez (Bolivia), were studied.

The Bolivian sand was analyzed by X-ray fluorescence in order to determine its major elements. The elements found were: Al, Si, P, S, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Sr, Zr, Ba and Pb, with a predominance of Si and Fe. Chemical analysis of the Brazilian mineral was supplied by Minas Gerais. Al, Si, S, K and Fe (as the predominant components) and Mn, Ag, Au and As (as the minor components) were detected. The mineralogical analysis of the same sample found quartz, silicates, mica and pyrites as the major minerals.

The Bolivia sand, which contains a large amount

of Au in the form of small particles (“pellets”) was lixiviated without size reduction. Brazil mineral, containing a small amount of gold that was distributed uniformly, was crushed to a size of 100–200 mesh. Both samples were mechanically homogenized and dried at 110°C for 3 h, prior to the leaching process. Two samples containing 50 g of each mineral and sand were leached for 48 h with 100 ml of an alkaline solution containing 1000 ppm of NaCN. A 5-ml volume of the pulp was removed periodically, centrifuged, filtered and injected into the CE system.

### 3. Results

In process and environmental analysis, rapid and sensitive methods are needed. These required features prompted attempts to optimize the species separation in a short time and the limits of detection.

In a CE system, two of the main factors affecting the separation are the buffer composition and the pH. When working with real samples, NaCN has to be added to the buffer to stabilize some metal cyanides so, for security reasons, the pH value has to be kept over 10 to avoid  $\text{CN}^-$  volatilization. At this pH value, there is a high electroosmotic flow from the anode to the cathode so, to assure the detection of cyano complexes with quite different electrophoretic mobilities, the simplest method is to decrease the electroosmotic flow and work with a negative polarity. In this work, the cationic surfactant, TTAB, was used at concentrations under its critical micelle concentration [20] to control electroosmotic flow. Results obtained with different TTAB concentrations showed that working between  $1 \cdot 10^{-5}$  and  $5 \cdot 10^{-5}$  M was most appropriate for the separation. Fig. 1 shows that the separation of different cyano complexes from real samples is accomplished with analysis times of between 9 and 12 min, depending on the TTAB concentration.

In order to optimize the signal-to-noise ratio, and thus the limits of detection (LOD), the influence of some analytical parameters (buffer-to-sample conductivity ratio, injection time, detection wavelength, applied voltage and buffer adsorptivity) to maximize signal and minimize noise have been studied. The best results were obtained for an applied voltage of

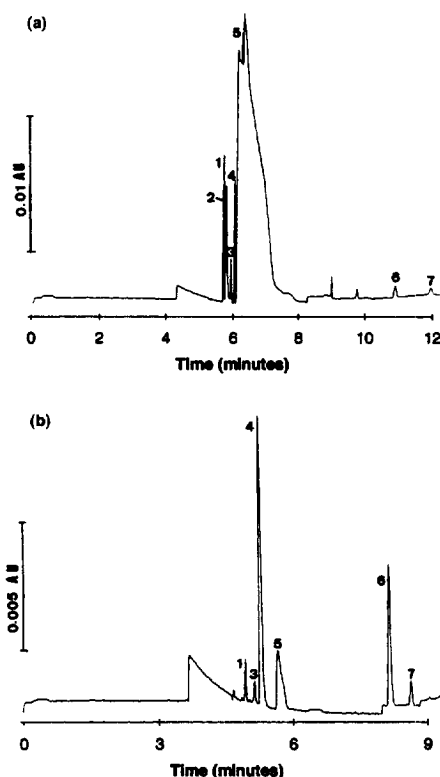


Fig. 1. Electropherograms of leaching solutions from (A) the Brazilian mineral and (B) the Bolivian sand. Analytical conditions: Buffer, 20 mM  $\text{Na}_2\text{HPO}_4$ , 36 mM NaCl, 1 mM NaCN, 10  $\mu\text{M}$  (for A) and 30  $\mu\text{M}$  (for B) TTAB (pH=11). Constant voltage,  $-12$  kV. Fused-silica column (58 cm $\times$ 0.05 mm I.D.) and 32 cm to detector. Injection time, 30 s. Detection wavelength, 204 nm. 1= $\text{Cu}(\text{CN})_3^{2-}$ ; 2= $\text{HS}^-$ ; 3= $\text{Ni}(\text{CN})_4^{2-}$ ; 4= $\text{Fe}(\text{CN})_6^{3-}$ ; 5= $\text{SCN}^-$ ; 6= $\text{Au}(\text{CN})_2^-$  and 7= $\text{Ag}(\text{CN})_2^-$

$-9$  kV, a detection wavelength of 204 nm and a buffer composition of 20 mM  $\text{Na}_2\text{HPO}_4$ , 36 mM NaCl, 1 mM NaCN and 10  $\mu\text{M}$  TTAB.

By using the optimized analytical conditions, the detection limits were calculated for two different sample matrices, to simulate a waste water at pH 11 and a leaching solution, at different injection times (see Table 1).

It can be seen that for the low conductivity sample matrix, the limits of detection are lower because of the stacking process, and that the influence of the injection time on the limits of detection is smaller when working at high injection times, probably due to the concentration gradient formed during the injection time [21].

Table 1

Limits of detection (LOD) for metal cyanides and  $\text{SCN}^-$  for different matrices and injection times ( $t_{inj}$ )

Matrix	$t_{inj}$ (s)	LOD (ppb)					
		Cu(I)	Ni(II)	Fe(II)	$\text{SCN}^-$	Au(I)	Ag(I)
NaOH, pH 11	100	6	8	10	10	80	16
NaOH, pH 11	50	8	13	12	18	80	25
500 ppm NaCN	50	20	32	65	110	110	35
500 ppm NaCN	25	40	70	90	115	205	70

### 3.1. Application to real samples

The leaching process is one of the stages in the recovery of gold from ores by cyanidation that needs to be analytically controlled. Therefore, the developed CE method was used to follow the evolution of leaching kinetics for two different real samples, a gold mineral from Brazil and a gold sand from Bolivia, to prove its capacity for monitoring the formation of the gold cyanide complex under leaching conditions.

The first step in this application is the identification of metal–cyano complexes in the real samples. This was accomplished by the addition of standards to the leaching solutions, obtained after a contact time of 24 h for the NaCN solution with the Brazilian mineral and 48 h with the Bolivian sand, and their injection to the CE system (see Fig. 1). Thiocyanate and the cyano complexes  $\text{Au}(\text{CN})_2^-$ ,  $\text{Ag}(\text{CN})_2^-$ ,  $\text{Cu}(\text{CN})_3^{2-}$ ,  $\text{Ni}(\text{CN})_4^{2-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  were identified in both samples, whereas  $\text{HS}^-$  only appears in the Brazilian mineral.

Once metal–cyano complexes in leaching solutions from real samples were identified, a study of the leaching kinetics was carried out. The leaching process was performed in duplicate for each sample, and all obtained values correspond to the average of two analytical measurements over the same replica. Results obtained for the Brazilian mineral and for the Bolivian sand are shown in Figs. 2 and 3, respectively. It can be seen that the amount of Au in the two duplicates was the same after 8 h of leaching in the Brazilian mineral, whereas the results for the Bolivian sand showed differences between the duplicates, which remained constant throughout the whole leaching time. These differences are attributable to the presence of pellets in the Bolivian samples, giving poor homogeneity in duplicates, and to a

more uniform distribution of gold in the crushed Brazilian mineral. The deviation found for Fe(II) in the Brazilian sample at a leaching time of 24 h can be explained because the resolution between the Fe–cyanide complex and  $\text{SCN}^-$  decreases with leaching time, due to the high amount of  $\text{SCN}^-$  in the sample, making quantitative measurements difficult.

On the other hand, the evolution of concentration with time is similar for both samples, and there is no significant increase in the amount extracted between 8 and 48 h, verifying that the leaching processes with NaCN occur within a few hours.

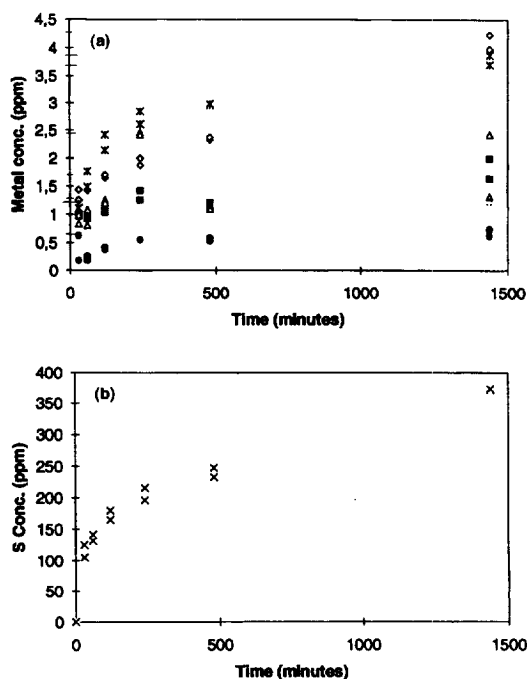


Fig. 2. Evolution of metal concentration as a function of time for leaching solutions from Brazilian mineral. \*, Au(I); ●, Ag(I); △, Fe(II); ◇, Cu(I); □, Ni(II) and ×,  $\text{SCN}^-$ .

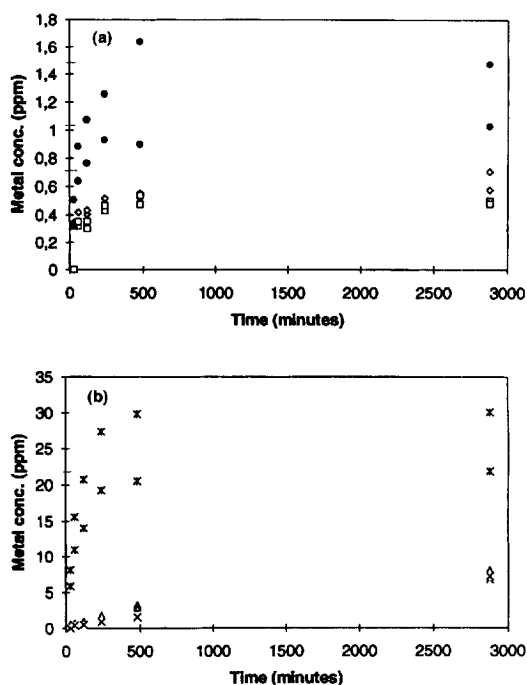


Fig. 3. Evolution of metal concentration as a function of time for leaching solutions from Bolivian sand. The assignment of compounds is the same as in Fig. 2.

The Au–cyano complex is the predominant compound in the leaching solution from the Bolivian sand (25 ppm were achieved after 48 h, compared with 0.4–5 ppm of other compounds), whereas the presence of other metal–cyano complexes is more important in the leaching solution from the Brazilian mineral (all metals range between 1 and 3 ppm after 24 h of leaching).

The presence of the different metal–cyano complexes and  $\text{SCN}^-$  agrees with the characterization data of the solids. The remainder of the metals and non-metals that are in the original solid samples, either do not form cyano complexes (e.g. Al, As, P, Si and Sr [4]) or form weak and undetectable cyano complexes (e.g. Zn and Mn [22]).

The high concentration of  $\text{SCN}^-$  in the Brazilian mineral is attributed to the high kinetics of dissolution of the pyrrhotite that is present at a level of 1.5% in the mineral. The dissolution of pyrrhotite in a basic medium results in the formation of  $\text{HS}^-$ , which reacts with the  $\text{CN}^-$  in the buffer, giving  $\text{SCN}^-$ .

Table 2

Metal concentrations (in ppm) after 24 h of leaching the Brazilian mineral, measured with two different analytical systems (CE and ICP).

	Ag	Au	Cu	Fe	Ni
CE	0.58	3.23	3.00	7.85	1.61
ICP	0.54	3.26	2.92	6.38	1.54

Finally, the analysis of the leaching solutions by ICP ratifies the presence of the different metals and S, and gave quantitative results for metals that were very close to those obtained by CE (see Table 2).

### Acknowledgments

The authors are grateful to Erny Lauro Meinhardt for his valuable help and useful advice. This work was financially supported by the CICYT (Project No. AMB93-0484), Ministry of Science and Education of Spain and by a scholarship from Comisionat per a Universitats i Recerca (Generalitat de Catalunya).

### References

- [1] F. Habashi, *CIM Bull.*, 80 (1987) 108.
- [2] J. Marsden and I. House, *The Chemistry of Gold Extraction*, Ellis Horwood, New York, NY, 1992.
- [3] J.C. Yannopoulos, *The Extractive Metallurgy of Gold*, Van Nostrand, New York, NY, 1991.
- [4] A.G. Sharpe, *The Chemistry of Cyanocomplexes of the Transition Metals*, Academic Press, London, 1976.
- [5] R.J. Coombes and A. Chow, *Talanta*, 26 (1979) 991.
- [6] R.R. Brooks, J. Holzbecher, D.E. Ryan, H.F. Zhang and A.K. Chatterjee, *Atom. Spectrosc.*, 2 (1981) 151.
- [7] G. Steffer and J. Luck, *Spectro Report*, Application Note 51/2, Spectro, Kleve, 1991.
- [8] P. McCarthy and R.W. Klusman, *Anal. Chem.*, 65 (1993) 244R.
- [9] C. Pohlandt, *S. Afr. J. Chem.*, 38 (1985) 110.
- [10] I. Nomomura, *Anal. Chem.*, 59 (1987) 2073.
- [11] D.F. Hilton and P.R. Haddad, *J. Chromatogr.*, 361 (1986) 141.
- [12] B. Grigorova, S.A. Wright and M. Josephson, *J. Chromatogr.*, 410 (1987) 419.
- [13] P.R. Haddad and N.E. Rochester, *Anal. Chem.*, 60 (1988) 536.
- [14] L. Giroux and D.J. Barkley, *Can. J. Chem.*, 72 (1994) 269.
- [15] M. Aguilar, X. Huang and R. Zare, *J. Chromatogr.*, 480 (1989) 427.

- [16] M. Aguilar, A. Farran and M. Martínez, *J. Chromatogr.*, 635 (1993) 127.
- [17] W. Buchberger, O.P. Semenova and A.R. Timerbaev, *J. High Resolut. Chromatogr.*, 16 (1993) 153.
- [18] W. Buchberger and P.R. Haddad, *J. Chromatogr. A*, 687 (1994) 343.
- [19] V. Martí, M. Aguilar and E.S. Yeung, *J. Chromatogr. A*, 709 (1995) 367.
- [20] B. Baraj, M. Martínez, A. Sastre and M. Aguilar, *J. Chromatogr. A*, 695 (1995) 103.
- [21] D.S. Burgi and R.L. Chien, *Anal. Chem.*, 63 (1991) 1354.
- [22] J. Brigando, *Bull. Soc. Chim. Fran.*, 24 (1957) 503.