

Determination of gold(I) and silver(I) cyanide in ores by capillary zone electrophoresis

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(First received September 11th, 1992; revised manuscript received December 22nd, 1992)

ABSTRACT

Capillary zone electrophoresis (CZE) with on-column UV detection at 214 nm was used to detect and determine gold(I) and silver(I) cyanide complexes in alkaline cyanide solution. Under an applied voltage of 25 kV, dicyanoaurate(I) and dicyanoargentate(I) were separated in less than 6 min. Carbonate buffer was used and the separation of both anions was achieved using an anodic injection and cathodic detection scheme. The method was applied to the determination of gold and silver cyanide in ore samples. Quantitative analysis was possible and good agreement between CZE and atomic absorption spectrometric results was obtained.

INTRODUCTION

The recovery of gold and silver from ores is accomplished almost exclusively by cyanidation, which involves leaching of the crushed ore with an alkaline solution of sodium or potassium cyanide. In this process, precious metals and a number of base metals are converted into their soluble cyano complexes.

For many years, the determination of precious metals in ores has been accomplished by a wide variety of analytical methods, e.g., flame and electrothermal atomic absorption spectrometry [1,2], inductively coupled plasma atomic emission spectrometry [3], X-ray fluorescence [4] and neutron activation analysis [5]. The main disadvantages of these methods are their inability to differentiate between oxidation states of the same element, the occurrence of spectral interferences, the complexity of preparation of samples and the insufficient sensitivity.

Chromatographic techniques, however, do not

suffer from most of these disadvantages. For this reason some methods, which involve the conversion of precious metals into their anionic chloro or cyano complexes, have been developed either using ion chromatography [6,7] or reversed-phase ion-interaction chromatography [8-10] with conductimetric or spectrophotometric detection.

An important factor in assessing the suitability of a method for monitoring the concentration of precious metals in the leach solution, which typically consists of a mixture of cyanide complexes in excess of cyanide, is the separation between the base metals and the precious metals. This separation is achieved for the gold(I) cyano complex by using the mentioned chromatographic techniques, but some problems arise in the determination of the silver(I) complex [8].

An alternative approach to this problem is to use capillary zone electrophoresis (CZE), in which a narrow band of the sample is introduced into a capillary and subjected to electrokinetic separation. Previous results indicated that CZE is a powerful tool for the separation of many

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compounds, from small ions to **biomacromolecules** [11].

In this paper, the separation and determination of silver(I) and gold(I) cyano complexes by CZE in solutions containing high concentrations of free cyanide ion is described. The results were applied to the determination of individual metal cyanides in ores.

EXPERIMENTAL

Instrumentation

An ISCO (Lincoln, NE, USA) Model 3850 integrated capillary electrophoresis system equipped with an untreated fused-silica capillary (64 cm \times 50 μm I.D.) was used for the separation. Detection was carried out by on-column measurement of UV absorption at 214 nm at a position 34 cm from the cathode. Peak areas were measured by a Spectra-Physics (San Jose, CA, USA) SP-4270 integrator. The sample was introduced into the system by a split-flow manual injector (ISCO) using an HPLC-type syringe.

For the injection conditions adopted in this work, by using a total volume injected from the syringe of 5 μl , the volume of sample loaded into the capillary was 4.6 nl.

A Philips PW 1404 X-ray fluorescence spectrometer was used, with a rhodium X-ray tube operated at 60 kV and 50 mA, an LiF crystal and scintillation detection.

A Perkin-Elmer Model 2380 absorption spectrometer was used to determine the metal content in the aqueous phase by atomic absorption spectrometry (AAS).

Reagents

Stock standard solutions of metal cyano complexes were prepared by dissolution of an accurately weighed amount of the complexes in a 0.01 M solution of alkaline sodium cyanide, followed by dilution as required. Analytical-reagent grade potassium **dicyanoaurate(I)** and potassium **dicyanoargentate(I)** were obtained from Johnson **Matthey** Chemicals (Karlsruhe, Germany).

Aqueous cyanide solutions containing gold(I) and silver(I) cyanide complexes were examined qualitatively by UV spectrophotometry over a

range of free cyanide concentration between 0 and 0.1 M. The UV spectra obtained revealed the presence of only a single gold and silver cyanide complex [**Au(CN)₂⁻** and **Ag(CN)₂⁻**] in the aqueous phase, independent of the free cyanide concentration.

Sodium hydrogencarbonate, disodium tetraborate, sodium dihydrogenphosphate, sodium hydroxide from Merck (Darmstadt, Germany), ammonium chloride from Panreac (Barcelona, Spain) and water deionized with a **Milli-Q** system (Millipore) were used to prepare different buffers. The electrolyte and sample solutions were filtered through a 0.45- μm membrane filter from **Lida** (Kenosha, WI, USA) and were degassed by ultrasonication.

Procedure for electrophoresis

The capillary tube was filled with a buffer solution by a syringe purge that flushed the entire capillary in a few seconds, and both ends of the tube were dipped into electrode solutions. The sample was introduced into the system by a syringe and a high voltage was applied.

The typical CZE configuration was used, in which the sample is injected at the anode, the detector is placed near the cathode and the electroosmotic flow is from the anode to the cathode [12].

Sample preparation

All experiments were carried out by shaking mechanically in special stoppered glass tubes at 20°C. Two samples of approximately 5 g of each crushed ore were leached with 10 ml of an alkaline solution of 0.01 M NaCN for 100 h, which was sufficient to achieve complete recovery from the ores.

After phase separation with a high-speed centrifuge, leach solution was injected directly into the CZE system.

RESULTS AND DISCUSSION

Separation

In a CZE system, the main factors affecting the quality of separation are the buffer composition, the pH and the applied voltage [13,14].

In this work, four different buffers were tested

TABLE I

COMPARISON OF MIGRATION TIMES, NUMBER OF THEORETICAL PLATES AND RESOLUTION AMONG FOUR BUFFER SOLUTIONS AT A CONSTANT CONCENTRATION OF 0.01 M AND pH 9.6 AND AN APPLIED VOLTAGE OF 25 kV

Buffer solution	t_m (min)		N	R_s
	$\text{Ag}(\text{CN})_2^-$	$\text{Au}(\text{CN})_2^-$		
Ammonium	7.3	8.8	34000	2.2
Phosphate	7.6	8.6	280000	5.1
Borate	7.2	8.4	210000	5.4
Carbonate	5.3	5.8	430080	5.4

for the separation of the Au(I) and Ag(I) cyano complexes. The results obtained are given in Table I, where N was calculated at $16t_m^2w^{-2}$ as in liquid chromatography, where t_m and w are the migration time and the peak width, respectively. The resolution (R_s) was calculated as $2(t_{m_2} - t_{m_1})(w_1 + w_2)^{-1}$, where the subscripts 1 and 2 represent the $\text{Ag}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$ peaks, respectively. From these results it can be seen that the best separation, e.g., higher values of the number of theoretical plates (N) and resolution (R_s), in the shortest analysis time (t_m), was obtained by the carbonate buffer. The pH was 9.6 to maintain the free cyanide ion.

From this point, the influence of applied voltage on the separation was studied by using 0.01 M carbonate buffer at pH 9.6. As good results (Table II) were obtained for the five voltages tested, an applied voltage of 25 kV, which gave a complete separation of the two

TABLE II

COMPARISON OF MIGRATION TIMES AT DIFFERENT APPLIED VOLTAGES USING 0.01 M CARBONATE BUFFER AT pH 9.6

Voltage (kV)	t_m (min)		Electroosmotic flow ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
	$\text{Ag}(\text{CN})_2^-$	$\text{Au}(\text{CN})_2^-$	
10	13.8	15.4	4.8
15	9.1	6.7	5.0
20	6.7	7.5	5.7
25	5.3	5.8	7.4
30	4.2	4.7	7.9

cyano complexes in less than 6 min, was chosen. The values of the electroosmotic flow for each voltage are also shown in Table II.

Using the selected experimental conditions, the electropherogram in Fig. 1 was obtained, which seems to indicate that $\text{Ag}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$ migrate in this order toward the cathode, well separated from each other.

In order to understand the elution order, it has to take into account that the electrophoretic mobility depends on the charge, shape and size of the analyte.

Au(I) and Ag(I) cyano complexes are linear, singly charged anions [$\text{Au}(\text{CN})_2^-$, $\text{Ag}(\text{CN})_2^-$], so the only difference is in their anionic volume. The elution order can be rationalized by the fact that $\text{Au}(\text{CN})_2^-$ seems to be a poorly hydrated anion compared with $\text{Ag}(\text{CN})_2^-$ [15]. This difference was ascribed by Nyholm [16] to the large s-p separation energy for gold(I). Hence this lowest hydration will reduce the size of the moving ion. This size reduction may result in greater electrophoretic migration and, accordingly, retardation.

Quantification

Detection limits were calculated as the amount of sample equivalent to a signal due to the analyte equal to three times the standard deviation of a series of ten replicate measurements of

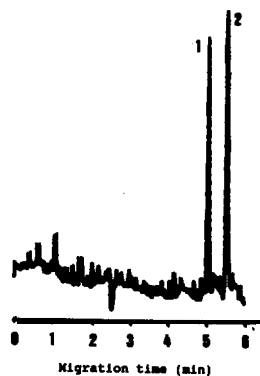


Fig. 1. Electropherogram of a mixture of $\text{Ag}(\text{CN})_2^-$ and $\text{Au}(\text{CN})_2^-$ standards in excess of cyanide. Capillary fused-silica column (64 cm \times 50 μm I.D.); carbonate buffer, 0.01 M (pH 9.6); applied voltage, 25 kV; injection volume, 4.6 nl; sample amount, 80 pg Ag and 65 pg Au. Peak assignment: 1 = $\text{Ag}(\text{CN})_2^-$; 2 = $\text{Au}(\text{CN})_2^-$.

a reagent blank signal [17]. The results obtained were 13 pg for Au and 16 pg for Ag, which correspond to 2.82 and 3.48 **pg/nl**, respectively.

The relative standard deviation for ten replicate injections of 164 pg of gold and silver, as the dicyanoaurate(I) and the dicyanoargentate(I) complexes, were 6.6% and 4.0% respectively.

The two samples provided good linearity in the concentration range 20-250 pg. The equations of the straight lines obtained by linear regression were $A = -297.6 + 98.1C$ ($r = 0.995$) for Au and $A = -13.5 + 61.8C$ ($r = 0.995$) for Ag, where A is the peak area and C the sample amount in pg.

Application to ore samples

On the basis of the results obtained for the dicyanoaurate(I) and the dicyanoargentate(I) standards, the application of the CZE method to the determination of gold and silver in ore samples was attempted. Two samples from two different sources, a gold mine of Bolivia and a silver mine of Spain, were analysed.

First, these samples were qualitatively analysed by X-ray fluorescence in order to determine their majority elements. The elements found in the Bolivian sample were Al, Si, **P**, S, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Sr, Zr, Ba and Pb, the predominant components being Si and Fe. The elements found in the Spanish sample were Al, Si, **P**, S, K, Ca, Mn, Fe, Ti, Cu, Zn, As, Sb, Zr, Ba and Pb, the predominant components being Si, **P**, S, K, Fe, As, Ba and Pb.

One interesting observation is that X-ray fluorescence does not have sufficient sensitivity to detect the presence of Au or Ag in the samples. On the other hand, it can be observed that there are some elements capable of forming cyano complexes, *i.e.*, Ag, Au, Cu, Fe, Mn and Zn [8], so after the sample treatment the leach solutions will consist on a mixture of metal cyan0 complexes in excess of cyanide.

In order to determine gold and silver in the samples, the leach solutions were injected directly into the CZE system and the **electropherograms** in Fig. 2 were obtained. It can be seen that for the Bolivian sample **only** one peak, which corresponds to the gold(I) cyano complex, was obtained, and that for the Spanish sample

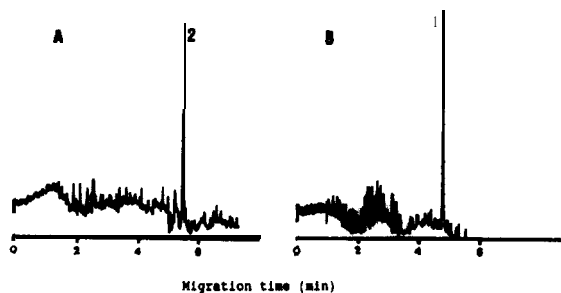


Fig. 2. Electropherograms of leach solutions of (A) Bolivian and (B) Spanish ore. Experimental conditions as in Fig. 1.

the peak obtained corresponds to the silver(I) complex. Further, no other signal corresponding to the base metal cyano complexes was observed.

In order to understand these results, it has to be borne in mind that the different complexes have different negative charges. The Au(I) and **Ag(I)** cyano complexes have one negative charge, whereas the other cyano complexes have between two and four negative charges. The ionic mobilities of these highly negatively charged metal cyanides would be greater than the electroosmotic flow, so to detect them it would be necessary to inverse the polarity of the power supply [18].

From the electropherograms in Fig. 2, the gold and silver contents in the two samples were determined. The results are given in Table III together with those obtained for the same leach solutions using **AAS**. Excellent agreement between the two methods was obtained. As **AAS** gives the total metal concentration for each

TABLE III
COMPARISON BETWEEN THE RESULTS OBTAINED FOR THE SAME LEACH SOLUTIONS USING CZE AND AAS

The results are given as averages for duplicate samples in mg metal/kg ore.

Ore sample	CZE		AAS	
	Au	Ag	Au	Ag
Bolivian	29.90	ND ^a	28.26	ND
Spanish	ND	39.80	ND	41.92

^a ND = Not determined.

element, this agreement signifies that all the Au and Ag present in the sample are in form of dicyano complexes, and that no other cyano complex of these metals was formed under the experimental conditions used.

CONCLUSIONS

The CZE method developed allows the rapid separation of Au(I) and Ag(I) cyano complexes in leach solutions from ore samples. The leach solutions obtained from the leaching can be introduced directly into the CZE system, without further treatment.

A major advantage of this method over spectrometric methods is its ability to monitor individual precious metal cyanide species. It has the advantage over chromatographic procedures of no interference from the base metals and also the separation of the silver(I) complex.

Further studies are being directed towards the determination and separation of metal cyano complexes, which are commonly present in cyanide leach solutions together with gold and silver complexes, such as zinc, iron and copper complexes, by CZE.

ACKNOWLEDGEMENT

Financial support provided by the CICYT (Project No. **NAT-1089**), Ministry of Science and Education of Spain, is gratefully acknowledged.

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