

The procedure was then extended to the analysis of a sample of poppy straw, opium and opium dross. The materials were extracted with either lime-water, acetic acid or ethanol–chloroform and analysed by MEKC and HPLC. The levels of the alkaloids determined by MEKC and HPLC are displayed in Table 2 and are in good agreement. The different levels of alkaloids extracted from the poppy straw with the lime-water and the solvent extraction were due to the different extraction conditions used. Similar alkaloid profiles were obtained when the poppy straw was extracted with acetic acid. Partial electropherograms showing the excellent separation of the alkaloids in the opium and opium dross extracts are displayed in Fig. 4.

#### 4. Conclusion

A rapid method for the separation and determination of alkaloids present in crude morphine, poppy straw and opium preparations by MEKC is described. The instrument repeatability for area calculation was acceptable, and the levels of the alkaloids in the samples were in good agreement with the levels determined by HPLC. The MEKC procedure is also faster and less costly to operate than the HPLC method.

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## Determination of chloride complex of Au(III) by capillary zone electrophoresis with direct UV detection

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### Abstract

Capillary zone electrophoresis was used for the determination of gold(III) chloride using direct UV detection at 220 nm. By using a capillary column 70 cm long, the optimum applied voltage was found to be around  $-7$  kV; carrier solution containing  $0.1$  M HCl and  $0.4$  M NaCl was used as an additive. At this pH, the electroosmotic flow-rate appears to be almost zero. The effects of chloride concentration and the applied voltage on determination efficiency are discussed. Heat generation appeared negligible as the electric current and migration time were reproducible. The analytical performance is discussed in terms of the detection limit, linearity and reproducibility. A single trial was performed in 18 min. Under these conditions, Pd(II) and Pt(IV) can also be determined; the order of mobility in the electropherogram was as follows:  $\text{PdCl}_4^{2-} > \text{PtCl}_6^{2-} > \text{AuCl}_4^-$ . The method was applied to the monitoring of Au concentration during a study of  $\text{AuCl}_4^-$  transport through solid-supported liquid membranes.

### 1. Introduction

In the last 5 years, the number of applications of capillary zone electrophoresis (CZE) has increased greatly, but the number of papers discussing CZE separations of inorganic cations has remained relatively low [1–3]. This technique offers rapid and efficient separation, being more matrix-independent than other existing techniques. Several ligands have been proposed for CZE analysis, including cyanide [4–6], EDTA [7,8], 8-hydroxyquinoline-5-sulfonic acid [9] and  $\alpha$ -hydroxyisobutyric acid [10]. In each case, methods using a mainly basic or slightly acidic medium were described. Methods em-

ployed for the determination of Au are both numerous and heterogeneous [11–14]. Many use dyes as complexing agents following an extraction step, which makes the procedure time consuming and tedious. Atomic absorption spectrometry (AAS) or inductively coupled plasma spectrometry is currently used [15,16].

In a study by Aguilar et al. [6], cyanide was used as a ligand for the determination of gold(I) and silver(I) at pH 9.6 by CZE. The samples and carrier solution were prepared with almost the same conductivity, and consequently the stacking effect was not used. In addition, the ionic strength ( $0.01$  M NaCN) was much lower than in the present work.

In this paper, the determination of gold(III) as the  $\text{AuCl}_4^-$  complex is described. The formation of the gold chloride complex is supported by using HCl and NaCl in the carrier solution (pH

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1) and in sample preparation (pH 1–2). A high ionic strength is usually undesirable since Joule heat is generated. To avoid this effect, a relatively moderate voltage was applied (below –10 kV). Enhancement of the detection limits was achieved by using stacking conditions.

The choice of low pH and high chloride concentration has two distinct advantages: (a) the gold(III) chloride complex is the predominant species and (b) as gold samples are normally dissolved in a strongly acidic medium, their determination by this procedure is convenient. The method was applied to the monitoring of Au concentration during a study of  $\text{AuCl}_4^-$  transport through solid-supported liquid membranes. Results obtained by CZE were compared with those of AAS analysis.

## 2. Experimental

### 2.1. Instrumentation

An 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 with an unmodified fused-silica capillary column, 70 cm (50 cm to the UV detector)  $\times$  0.05 mm I.D. A Model 4270 integrator (Spectra-Physics, San José, CA, USA), was used to record all data. A Shimadzu UV-240 UV-Vis recording spectrophotometer was used to record the absorption spectra of the gold(III) chloride complex. The pH and the conductivity of the solutions were monitored with a Crison-Digilab 517 pH meter and a Crison 525 conductimeter, respectively. A Perkin-Elmer Model 2380 AAS system was used to determine the total concentration (by flame) of Au in the samples.

### 2.2. Reagents and solutions

A chloride stock standard solution of Au(III) was purchased from Merck. All other reagents were of analytical-reagent grade from Merck.

Purified (18 M $\Omega$ ) water, obtained using a Millipore Milli-Q water-purification system, was used to prepare all solutions. All solutions were filtered through a 0.45- $\mu\text{m}$  membrane filter and degassed by ultrasound.

The carrier solution contained 0.1 M HCl and 0.4 M NaCl (conductivity ca. 65 mS  $\text{cm}^{-1}$ ) and the samples were prepared with 10–70% carrier solution (conductivity 8–50 mS  $\text{cm}^{-1}$ ).

### 2.3. Procedure for electrophoresis

The capillary tube was rinsed several times with deionized water, then equilibrated with carrier solution for 40 min before the first run. Both ends were dipped into two separate beakers filled with the same carrier solution. The sample solution was introduced into the cathodic end of the capillary by vacuum injection. Lastly, a negative voltage was applied. For determination of the electroosmotic flow-rate, negative and positive voltages were applied (using methanol as a marker). When finished, the CZE system must be cleaned carefully as the carrier solution used is corrosive.

## 3. Results and discussion

### 3.1. Gold chloride complex

Gold(III) produces species which are generally stable. Thus, gold(III) forms mixed complexes of chloride and hydroxide [17,18], depending on the pH and chloride concentration. The distribution diagram of Au(III),  $\text{H}^+$  and  $\text{Cl}^-$  species in Fig. 1 shows that  $\text{AuCl}_4^-$  is the predominant species at pH 1–2 for  $\text{Cl}^-$  concentrations higher than 0.01 M [19,20]. The absorption spectrum of this species (in 0.1 M HCl) showed a maximum around 220 nm, which is suitable for CZE determination with a UV detector.

### 3.2. CZE separation

In order to prevent hydrolysis of the chloride complex of Au(III), the pH of the carrier electrolyte was kept around 1 (0.1 M HCl), while 0.4

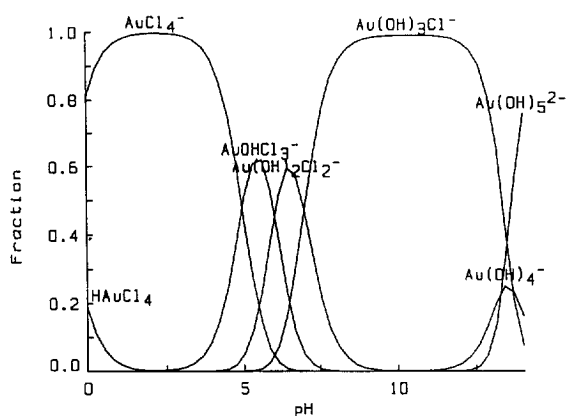


Fig. 1. Distribution species–pH diagram. Total gold(III) concentration,  $10 \mu\text{g ml}^{-1}$ ;  $0.1 \text{ M Cl}^{-}$ .

$M$  sodium chloride was used as an additive. At such a high ionic strength, some optimization of the applied voltage was required to obtain low noise and a stable electric current, which could be affected by Joule heat generation. It was observed that it was not possible to increase the voltage beyond  $-10 \text{ kV}$ , as the electric current was beyond the instrument limit. In addition, at  $-10 \text{ kV}$  applied voltage we noted an up-scale excursion of the baseline (detector drift). A voltage of  $-7$  to  $-8 \text{ kV}$  proved to be the best compromise between the applied voltage, migration time, sensitivity and baseline noise. We also noted that at  $-7 \text{ kV}$  applied voltage the reproducibility of the migration time was very good and the current through the capillary was fairly stable ( $190 \mu\text{A}$ ). This means that under the conditions used the Joule heating was negligible.

Gold samples were prepared in 10–70% carrier solution. Consequently, in all cases the conductivity of the sample was lower than that of the carrier solution, allowing the possibility of working in stacking conditions [21,22]. Under the conditions used ( $\text{pH} \approx 1$ ), silanols on the capillary wall become more protonated as the buffer pH is made more acidic, thereby reducing the charge on the capillary walls. Correspondingly, the electroosmotic flow should also be minimal or approach zero [23,24]. This was confirmed by the fact that we were not able to detect the methanol injected (as a marker) even when

applying a positive or negative voltage. Thus, the electrophoretic mobility rate of  $\text{AuCl}_4^{-}$  at  $\text{pH} 1$ , neglecting any small residual electroosmotic mobility, can be estimated using the equation

$$\mu_{\text{ep}} = LL_d/Vt_m \quad (1)$$

where  $L$  is the capillary length,  $L_d$  is the capillary length to the detector cell,  $V$  is the applied voltage and  $t_m$  is the observed migration time. According to Eq. 1, the electrophoretic mobility of  $\text{AuCl}_4^{-}$  is  $-4.5 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

Working at high ionic strength and low pH should yield a more reproducible separation, since changes in ionic strength and pH can cause significant changes in the magnitude of the electroosmotic flow. In contrast, separations that depend solely on the electrophoretic mobility are not subject to these flow variations [23]. The applied voltage can be increased when using a carrier solution containing  $0.1 \text{ M Cl}^{-}$ . Consequently, the migration time of the gold complex will be shorter. Under these conditions the samples have to be prepared in 100% carrier solution to avoid the instability of the  $\text{AuCl}_4^{-}$ , but the system will not work under stacking conditions, which improve the sensitivity and resolution.

It is also possible to determine Pd(II) and Pt(IV) simultaneously at  $270 \text{ nm}$  (to be published elsewhere), while at  $220 \text{ nm}$  all three can be determined simultaneously (Fig. 2). Nevertheless, the sensitivity of Pd(II) at this wavelength is about twice that at  $270 \text{ nm}$ , while the sensitivity of Pt(IV) is approximately three times lower.

### 3.3. Calibration graph, detection limit and reproducibility

Several calibration graphs were obtained by changing the concentration of the carrier solution (10–70%) in the prepared standards. At high sample-solution conductivity, the peak is broad and the sampling time is therefore limited. From preliminary experiments the following upper limits were selected: 20-s sampling time for samples containing 50–70% carrier solution

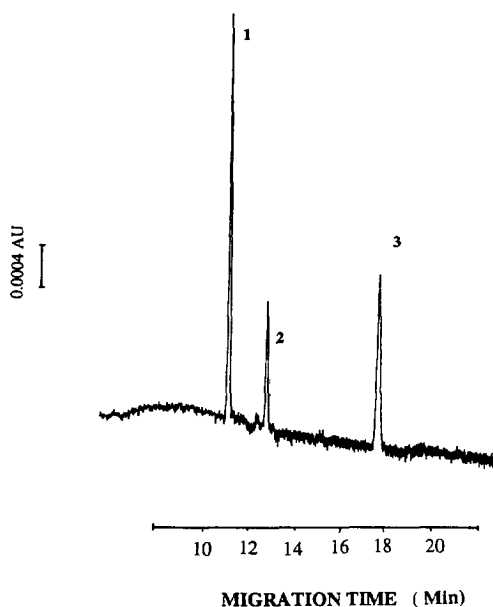


Fig. 2. Electropherogram obtained for a mixture of standard chloride complexes of Pd(II), Pt(IV) and Au(III). Conditions: capillary, 70 cm (50 cm to detector); carrier solution, 0.1 M HCl–0.4 M NaCl; voltage, –7 kV; UV detection at 220 nm; sampling time, 10 s. Sample contained 40% carrier solution. Peaks: 1 = Pd(II),  $5 \mu\text{g ml}^{-1}$ ; 2 = Pt(IV),  $10 \mu\text{g ml}^{-1}$ ; 3 = Au(III),  $4 \mu\text{g ml}^{-1}$ .

and 50 s for the rest. Fig. 3 shows that by decreasing the concentration of carrier solution in the sample, the peaks obtained are sharper, owing to the improvement achieved through stacking conditions. A linear relationship between the peak area or peak height and gold concentration in the range  $0.5\text{--}25 \mu\text{g/ml}$  was observed under all conditions for the calibration graphs tested ( $r = 0.991\text{--}0.999$ ). The good correlation indicates that this method can be used for samples having a conductivity in the range  $8\text{--}50 \text{ mS cm}^{-1}$  (10–70% carrier solution in the sample). In the case where the gold sample is prepared in less than 10% carrier solution, a decrease in the area of the  $\text{AuCl}_4^-$  peak was observed owing to the formation of hydrolysis species, which occurs at higher pH and lower chloride concentration [19]. For samples prepared in more than 70% of carrier solution, however, the peak was broad owing to the high sample conductivity (Fig. 3, peak 1). The detec-

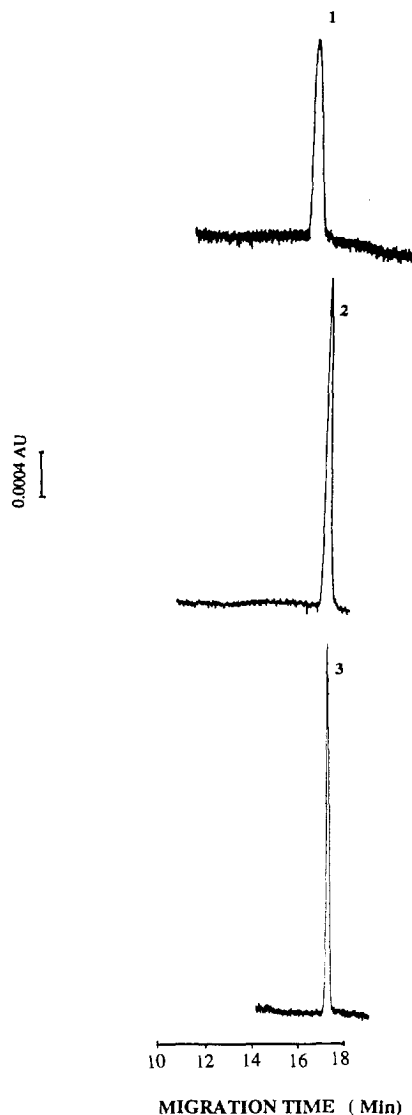


Fig. 3. Electropherograms of  $\text{Au}(\text{Cl})_4^-$  standard samples prepared at different concentrations of carrier solution. Conditions: sampling time, 20 s; other conditions as in Fig. 2. Sample preparation: (peak 1)  $5 \mu\text{g ml}^{-1}$  Au(III) dissolved in carrier solution; (peak 2)  $5 \mu\text{g ml}^{-1}$  Au(III) containing 50% carrier solution; (peak 3)  $4 \mu\text{g ml}^{-1}$  Au(III) containing 10% carrier solution.

tion limits for the different experiments performed are given in Table 1. A factor of two is often used in CZE to calculate the detection limit relative to the baseline noise; we used a factor of three [25]. A linear relationship was