Selective Extraction and Voltammetric Determination of Gold at a Chemically Modified Carbon Paste Electrode

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A sensitive chemically modified electrode for measuring gold by differential-pulse voltammetry is described. The electrode is prepared by dissolving triisooctylamine in carbon paste. Because of the selective extraction of gold, most of the common metal ions do not interfere with the stripping voltammetric measurements. The electrode was used to determine gold in authentic mineral samples without pre-isolation. The calibration plots are linear over the concentration range 0.1–10 µg ml^{-1} and the detection limit was found to be 0.03 µg ml^{-1} after a 15 min accumulation period. The preparation and electrochemical properties of the electrode were studied and the mechanism of the accumulation of gold at the modified electrode is discussed.

Keywords: *Gold determination; triisooctylamine; voltammetry; chemically modified electrode; carbon paste electrode*

Chemically modified carbon paste electrodes have received increasing attention recently. They are fabricated by mixing graphite powder, an organic liquid and a modifying agent. The resulting electrodes are inexpensive, easy to prepare and renew, have a relatively wide potential range and low background currents. They have been widely used in electrocatalysis, fouling protection and analyte preconcentration.[1,2] A number of studies on the use of chemically modified carbon paste electrodes for analytical measurements of metal ions by stripping voltammetry have been reported.[3-11] The very high sensitivity and greatly improved selectivity of these measurements are attributed to the formation of a metal–modifier complex and its accumulation in the electrodes.

The liquid–liquid extraction of carbon paste electrodes for some organic compounds has been studied.[12] It is possible that some extractants could be incorporated in the carbon paste electrodes to enhance the sensitivity and selectivity of the voltammetric determination. This paper describes a chemically modified carbon paste electrode, which can be used to extract and accumulate inorganic ions from dilute solution. The modifier chosen was triisooctylamine. Because this compound is well known for its selective extraction of gold,[13,14] the modified electrode shows high sensitivity and selectivity in differential-pulse stripping voltammetry. The electrode was used to measure the gold content in mineral ores without any pre-isolation. The fundamental relationships between parameters such as the modifier content, preconcentration time, concentration and voltammetric current were evaluated. The mechanism of electrode extraction was studied by means of ultraviolet (UV) spectrophotometry.

Experimental

Apparatus

Differential-pulse voltammetric determinations were performed with a Bioanalytical Systems (BAS) BAS-100A electrochemical analyser. A BAS PL-10 digital plotter and an Epson LQ-1600 printer were used for recording the voltammograms and experimental data. The cell used was a BAS Model VC-2 voltammetric cell of 10 ml volume. The working electrode, reference electrode (Ag–AgCl, BAS Model RE-1) and platinum wire auxiliary electrode were introduced into the cell through holes in the Teflon cover. A BAS C-1A cell stand provided magnetic stirring during the accumulation period. A Shimadzu UV-265 spectrophotometer was used to obtain absorption spectra. Photographs of the electrode surface were taken by means of a Hitachi SEM-570 scanning electron microscope.

Reagents

Triisooctylamine, $N[(CH_2)_7CH_3]_3$, was obtained from Tokyo Kasei Organic Chemicals. The stock solutions of gold and of the other metal ions were 1 mg ml^{-1}. The supporting electrolyte solution was 0.1 mol l^{-1} HCl. All solutions were prepared from doubly distilled water.

Electrode Fabrication

The pure carbon paste electrode was obtained by thoroughly mixing 4.0 g of liquid paraffin (Shanghai Institute of Chemical Reagent) with 6.0 g of graphite powder (Fisher) and then packing the slurry mixture into the tube of the electrode. Modified carbon paste was prepared by mixing 1.2 g of triisooctylamine with 2.8 g of mineral oil. Uniform dispersion of the modifier was obtained by sonicating the mixed oil for 10 min. Finally, 6.0 g of graphite powder were added and mixed thoroughly with the triisooctylamine–paraffin oil mixture. A portion of the modified carbon paste was packed into the end of a glass tube (4 mm i.d.) and the electrode preparation was as described previously.[11]

Procedure

The electrode was immersed in the sample solution under open circuit for a given time. The solution was stirred with a magnetic bar (400 rev min^{-1}) during the preconcentration period. The electrode was then transferred into a 0.1 mol l^{-1} HCl solution and activated at +1.2 V for 30 s. Finally, differential-pulse voltammetric measurements were performed by scanning the potential from +0.8 to 0.0 V at a rate of 5 mV s^{-1}. A fresh and shiny surface was obtained by packing a little carbon paste onto the electrode tube and then polishing the surface with transparent paper.

Results and Discussion

Effect of Extraction

The pure carbon paste electrode and the chemically modified electrodes prepared with different amounts of triisooctylamine were examined under the same conditions (Fig. 1). After open circuit accumulation for 2 min in a stirred solution with 3 µg ml^{-1} of gold, the electrodes were removed, washed and then placed in a quiescent solution of 0.1 mol l^{-1} HCl for voltammetric determination. All modified electrodes showed clear stripping peaks of gold near a potential of +0.42 V (Fig. 1, curves B–E), whereas the pure carbon paste electrode did not show any voltammetric peak (Fig. 1, curve A). This can be
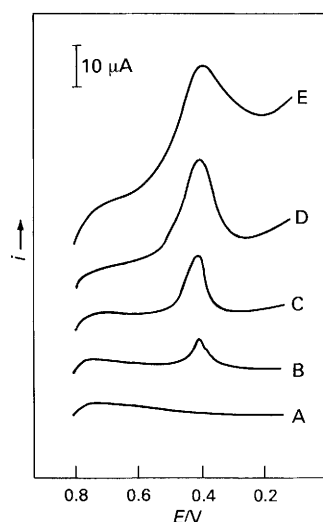
Fig. 1 Differential-pulse stripping voltammograms of A, a pure carbon paste electrode, and chemically modified electrodes with B, 4; C, 8; D, 12; and E, 16% triisooctylamine in a 3 µg ml^{-1} gold solution after 2 min open circuit accumulation. Supporting electrolyte solution, 0.01 mol l^{-1} HCl; scan rate, 5 mV s^{-1}; pulse amplitude, 50 mV; and pulse period, 0.5 s
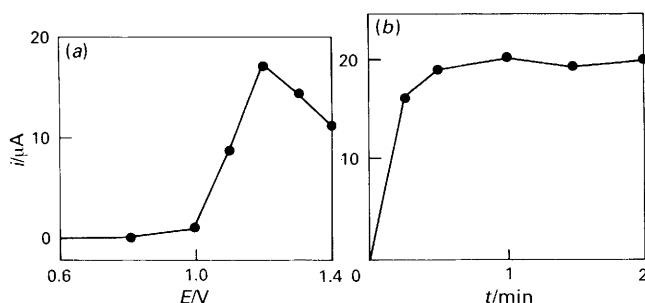
Fig. 2 Influence of (a) activation potential and (b) activation time on the stripping peak current of a 12% triisooctylamine carbon paste electrode in a 5 µg ml^{-1} gold solution after a 1 min accumulation period. Other conditions as in Fig. 1

Fig. 3 Influence of surface treatment on the response of the electrode in a 5 µg ml^{-1} gold solution after a 1 min accumulation period: A, cleaning with water; B, cleaning with 1 mol l^{-1} ammonia–ammonium chloride; C, cleaning with 1% thiocarbamide; D, cleaning with 1% sodium sulfide; and E, polishing the surface. Other conditions as in Fig. 2

explained by the fact that triisooctylamine extracted gold from the solution and accumulated the metal into the electrode; a voltammetric response was then obtained during the potential scan. The more triisooctylamine there is in the electrode, the greater the amount of gold extracted, i.e., the stripping current was enhanced with an increase in the amount of triisooctylamine. However, the peak was distorted if the content of the modifier was more than 12% (Fig. 1, curve E). Accordingly, a carbon paste electrode containing 12% triisooctylamine was used throughout, considering the requirements of sensitivity and peak shape.

The extraction ability of triisooctylamine in the electrodes was also examined by measuring the stripping current of gold at different depths below the surface. It was found that modified electrodes, from which 0.2 and 0.4 mm of the surface layer had been removed, still retained 35 and 12%, respectively, of the original voltammetric response (not shown). This demonstrated that the extracted gold was present not only on the surface, but also in the electrode itself. This feature is advantageous in enhancing the sensitivity of the electrode.

Activation of the Electrode

The surface of a modified electrode, which had extracted gold, did not show a voltammetric response in cathodic stripping voltammetry. In order to activate the electrode, pre-treatment was necessary. After application of a positive potential for a given period, the electrode became much more sensitive than an untreated electrode. Fig. 2 illustrates that the optimum
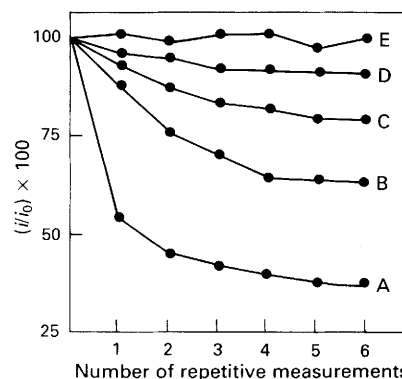
potential for this treatment is +1.2 V [Fig. 2(a)] and that the pre-treatment time should be not less than 30 s [Fig. 2(b)].

Electrode Cleaning and Precision

After each electrochemical determination, it is difficult to remove gold completely from the triisooctylamine modified carbon paste electrode by means of conventional potential-cleaning in stripping voltammetry, and this will lead to a lower result in subsequent measurements. Several chemical reagents, such as sodium sulfide, thiocarbamide and ammonia–ammonium chloride, were chosen in an attempt to remove gold from the electrode surface. Hence, after each measurement the electrode was soaked in a stirred solution of one of the above reagents for 2 min. Fig. 3 shows the results of six repetitive measurements. Solutions of 1% sodium sulfide and thiocarbamide were effective for renewal of the electrode; however, there was still a 12 and 21% decrease, respectively, in the peak current. A simple and effective method is to polish the electrode surface with filter-paper and then with a smoothed paper card. The first polishing with filter-paper removes the residue of gold and provides a fresh surface; the second polishing affords a shiny surface. The precision was examined from seven repeated measurements in a 5 µg ml^{-1} gold solution (1 min accumulation period). The mean peak current was 19.56 µA with a range of 18.86–20.04 µA. A relative standard deviation of 5.6% was found.

Instrumental Conditions

Various instrumental conditions, such as potential scan rate, and pulse amplitude and period, affect the peak current of gold in differential-pulse stripping voltammetry. Increasing the scan rate and pulse amplitude will cause an increase in the peak current and peak broadening; increasing the pulse period will cause a slight decrease in the current. Similar results have been reported previously.[15] A scan rate of 5 mV s^{-1}, a pulse amplitude of 50 mV and a pulse period of 0.5 s were chosen for maximum sensitivity and the best peak shape. The stirring rate used during the accumulation step also affects the resulting current. For example, a 2.8-fold peak enhancement was observed for a stirred solution (400 rev min^{-1}) compared with a quiescent solution (3 µg ml^{-1} of gold, 2 min accumulation period). It is obvious that stirring the solution increases the rate of transport of [AuCl$_4$]$^-$ anions to the electrode surface. Such mass-transport control indicates a fast rate of extraction of gold by triisooctylamine.

Accumulation Period

The dependence of the differential-pulse voltammetric peak current on accumulation time for different concentrations of

gold is shown in Fig. 4. At the lower concentration, 0.5 $\mu g\ ml^{-1}$, the response increased markedly as the accumulation time increased; the linearity between the peak current and time was maintained over a period of 15 min (slope, 1.98 $\mu A\ min^{-1}$; correlation coefficient, 0.999; Fig. 4, curve A). However, deviation from linearity was observed for solutions of higher concentration (Fig. 4, curves B and C). The linear relationship held for 6 min for a 1 $\mu g\ ml^{-1}$ solution but for only 3 min for a 3.5 $\mu g\ ml^{-1}$ solution. This indicated that the electrode was gradually becoming saturated with gold. Obviously, the use of a shorter accumulation time for a solution of high concentration will reduce the analysis time, while the use of a longer time for a solution of low concentration will enhance the sensitivity.

Calibration Plot and Detection Limit

The stripping peak current of the modified electrode increased with the concentration of gold. The response was linear over the concentration range 0.1–1.0 $\mu g\ ml^{-1}$ after an accumulation period of 2 min (slope, 0.98 μA per 0.1 $\mu g\ ml^{-1}$; correlation coefficient, 0.999; Fig. 5), and over the concentration range 1–10 $\mu g\ ml^{-1}$ after a 5 min accumulation period (slope, 5.9 μA per $\mu g\ ml^{-1}$; correlation coefficient, 0.997; not shown). The detectability was calculated from three measurements of 0.1 $\mu g\ ml^{-1}$ of gold after an open circuit preconcentration period of 15 min. The detection limit of the 12% triisooctylamine modified carbon paste electrode, calculated from a signal-to-noise ratio of 3, was found to be 0.03 $\mu g\ ml^{-1}$.

Interference of Metal Ions

The presence of metal ions in the sample solution is disadvantageous for stripping voltammetric analysis. However, most of the common metal ions do not interfere with the
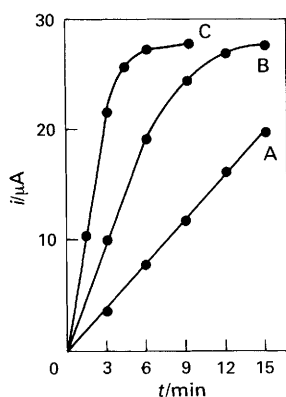
determination of gold using the proposed method. Table 1 shows that the results were still reproducible, even when 200 $\mu g\ ml^{-1}$ of Ca^{II} and Mg^{II}; 100 $\mu g\ ml^{-1}$ of Fe^{III} and Cu^{II}; 20 $\mu g\ ml^{-1}$ of Cd^{II}, Zn^{II}, Pb^{II}, Mn^{II} and Ni^{II} and 15 $\mu g\ ml^{-1}$ of Ag^{I} were added separately to a solution containing 2 $\mu g\ ml^{-1}$ of gold. Only a 3-fold excess of Pt^{IV} brought about a 9% increase in the peak current. The high selectivity of the electrode is attributed to the specific extraction properties of triisooctylamine, and to the open circuit preconcentration and medium exchange used in the method.[16] It is possible that the triisooctylamine modified electrode could be used in some complex samples without pre-isolation.

Application to the Analysis of Gold Mine Samples

The measurement of gold in mineral ores was demonstrated and the procedure was as follows. The weighed sample (1–10 g, depending on the gold content), from which the organic compounds had been removed by heating at 800 °C for 1 h, was mixed with 20 ml of water, 30 ml of concentrated HCl and 10 ml of concentrated HNO_3, then heated and evaporated to a volume of about 10 ml. The residual solution was diluted to 50 ml with 1 mol l^{-1} HCl and filtered. A 5 ml volume of the filtrate was diluted with 5 ml of water and used for the stripping voltammetric determination. The sample treatment procedure is relatively simple and involves no special separation. The results for the gold content, which are shown in Table 2, were in fairly good agreement with those obtained by atomic absorption spectrometry.

Discussion

In order to obtain an insight into the mechanism of the accumulation of gold at the electrode, the distribution coefficient (D) and extraction ratio (E) of gold were determined by the use of UV spectrophotometry.[17] A 10 ml volume of a 0.012 mol l^{-1} gold in HCl solution was extracted with 10 ml of a triisooctylamine solution in chloroform. The values of D and E obtained, viz., 15.1 and 93.8%, respectively, demonstrate that triisooctylamine is a very efficient reagent for extracting gold from aqueous solution.

The composition of the extracted species was examined by recording the extraction isotherm of gold in kerosene.[17] The triisooctylamine concentration was kept constant throughout the experiment at 0.0124 mol l^{-1}. When the gold concentration in the aqueous solution increased sharply, the organic solvent became saturated with gold. The gold concentration in kerosene reached 0.012 mol l^{-1} and did not increase further (Fig. 6). The ratio of the triisooctylamine and gold concentration in kerosene was approximately 1 : 1, which indicated that

Fig. 4 Influence of accumulation time on different concentrations of gold: A, 0.5; B, 1.0; and C, 3.5 $\mu g\ ml^{-1}$. Other conditions as in Fig. 2
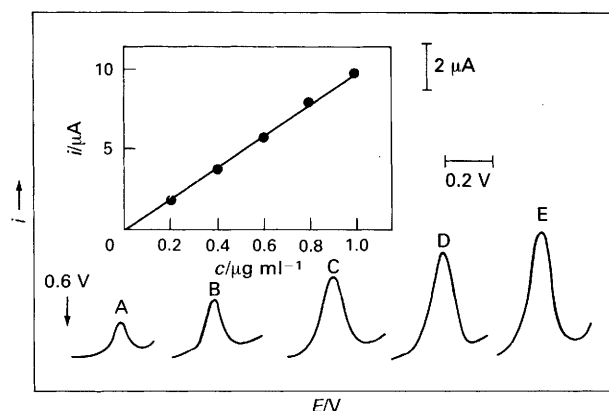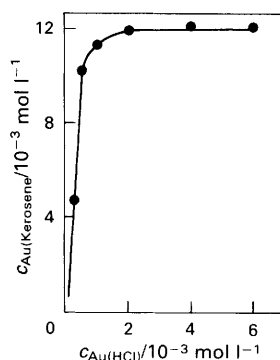

Fig. 5 Voltammograms for solutions containing increasing levels of gold, viz., 0.2–1.0 $\mu g\ ml^{-1}$ (A–E). Other conditions as in Fig. 2. Also shown (inset) is the resulting calibration plot

Table 1 Interference of some metal ions on the peak current in a 2.0 $\mu g\ ml^{-1}$ gold solution after a 2 min accumulation period

Species added	Concentration added/ $\mu g\ ml^{-1}$	Original current (i_0)/ μA	Current after addition (i)/μA	(i/i_0) $\times$ 100 (%)
Mg^{II}	200	21.85	21.62	98.9
Ca^{II}	200	21.97	22.28	101.4
Fe^{III}	100	22.10	21.54	97.5
Cu^{II}	100	21.82	21.75	99.7
Cd^{II}	20	21.66	21.84	100.8
Zn^{II}	20	22.05	21.75	98.6
Pb^{II}	20	21.63	21.94	101.4
Mn^{II}	20	22.12	22.42	101.3
Ni^{II}	20	21.45	21.92	102.2
Ag^{I}	15	22.21	21.63	97.4
Pt^{IV}	6	21.88	23.90	109.2

Table 2 Analysis of gold mine samples

	Stripping voltammetry				Atomic absorption spectrometry
Mineral ore	Original current/ μA	Gold added/ μg ml⁻¹	Current after addition/ μA	Content/ μg g⁻¹	Content/ μg g⁻¹
Sample No. 1 (5 g)	12.55, 12.32, 12.61	2.0	29.62, 30.58, 29.81	14.2	13.5
Sample No. 2 (10 g)	14.12, 13.68, 14.24	0.5	19.62, 20.28, 20.06	11.7	10.5

(a)   (b)

Fig. 7 Scanning electron micrographs of the electrode surface (60% graphite powder, 28% paraffin and 12% triisooctylamine): A, ×800, showing the microholes; and B, ×3000, showing one of the microholes in greater detail

Fig. 6 Extraction isotherm of gold in HCl solution extracted with 0.0124 mol l⁻¹ triisooctylamine in kerosene
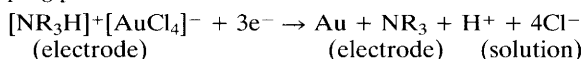
the extracted species contained one molecule of triisooctylamine and one gold ion.

In order to verify that gold ions were accumulated within the electrode itself, the electrode surface was studied by UV spectrophotometry after open circuit preconcentration for 10 min in a solution containing 20 μg ml⁻¹ of gold. A layer with a thickness of 0.2 mm was cut from the electrode surface and dissolved in 5 ml of chloroform. The solution was scanned from 400 to 190 nm and compared with a pure chloroform solution. The electrode containing 12% triisooctylamine without accumulation only gave an absorption peak of triisooctylamine at 282 nm. After accumulation, a new absorption peak at 315 nm was observed, which occurred in the solution containing [AuCl₄]⁻ anions (not shown). These phenomena suggested that gold was extracted into the electrode and formed an ion associate.[14] Scanning electron micrographs of the carbon paste surface are shown in Fig. 7. Numerous microholes were observed on the electrode surface, which had been carefully polished. It would appear that gold species are extracted into the electrode through these holes. Accordingly, the most likely electrode reactions are as follows:
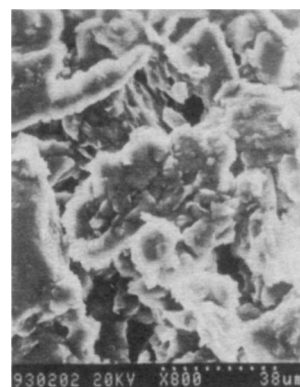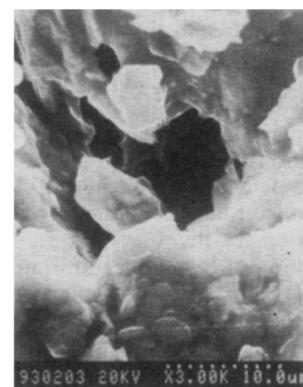
Preconcentration process:

$$NR_3 + HCl + [AuCl_4]^- \rightarrow [NR_3H]^+[AuCl_4]^- + Cl^-$$
(electrode) (solution)   (electrode)   (solution)

Stripping process:

$$[NR_3H]^+[AuCl_4]^- + 3e^- \rightarrow Au + NR_3 + H^+ + 4Cl^-$$
   (electrode)   (electrode)   (solution)

It is worth noting that the electrodes were not active during the potential scanning process after the accumulation of gold. The stripping peaks were obtained only after a treatment at a positive potential. This phenomenon is not yet fully understood. A possible explanation might be that the positive potential causes the ion associate ([NR₃H]⁺[AuCl₄]⁻) to dissociate; this potential then attracts the anions ([AuCl₄]⁻) close to the surface of the carbon particles from the paraffin oil. Finally, these anions are reduced to gold during the potential scanning process. The positive potential treatment activates the gold accumulated at the electrode and makes the reductive reaction much faster.

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