

Anodic Stripping Voltammetric Determination of Gold on a Polyvinylferrocene Coated Glassy Carbon Electrode

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The anodic stripping voltammetric determination of gold was accomplished on a chemically modified glassy carbon electrode in a solution containing chloride ions. A modifying polymer, polyvinylferrocene, was coated by immersing the glassy carbon surface in its solution in methylene chloride followed by solvent evaporation. Tetrahalo complexes of gold, tetrachloroaurate(III) and tetrabromoaurate(III) ions, were found to be reduced to metallic gold by chemical reduction during immersion of the polymer coated electrode into the solution containing aurate(III) ions. This reaction was utilized as means of preconcentration without the need for cathodic electrolysis prior to the anodic stripping of metallic gold. The effects of the preconcentration period, film thickness and the presence of Cu(II) ions as possible interferants were investigated.

Key Words: Polyvinylferrocene, modified electrode, gold determination, anodic stripping voltammetry, tetrahalo complexes of gold.

Introduction

Analysis of trace amounts of gold is important, especially in geological samples and underground waters. Anodic stripping voltammetry is an attractive trace analysis method due to its high sensitivity, low cost and on-line application possibility. Mercury cannot be used as an electrode material for the anodic stripping voltammetric determination of gold because of the lower oxidation potential of mercury compared with that of gold. A graphite or carbon paste electrode could be of use in this respect, but the limit of detection is not low enough due to the higher background currents on such surfaces. Another complication arises from the copresence of copper ions in the analysis medium, which cause a significant amount of interference. Copper ions should therefore be separated by solvent extraction prior to anodic stripping analysis. Chemically modified electrodes may be of some help in surmounting these problems faced during the analysis of gold [1-9].

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The anodic stripping determination of gold using the carbon paste electrode was first reported by Jacobs [1]. The potential of the carbon paste electrode during the plating cycle was held at +0.1 V vs. SCE. Carbon paste and glassy carbon electrodes modified with various agents were used for the determinations of gold. A carbon paste electrode modified with amberlite LA2 was used as the electrode that enabled the preconcentration of gold ions by cathodic electrolysis in chloride and bromide containing media, prior to anodic stripping [2]. The carbon paste electrode was modified with chelating resin (ammino-isopropylmercaptan-type-cross-linked chelating resins) for the cyclic voltammetric determination of gold. The gold(III) ion was accumulated on the surface of the modified electrode by the chelating effect of the modifier in the carbon paste, without application of a potential [3]. The ethylenediamine as a complexing agent for many metal ions was fixed to the humic acid. The product was used to prepare a chemically modified carbon paste electrode for the determination of the Au(III) ion [4]. The electrochemical determination of gold nanoparticles in colloidal solutions was carried out based on the effect of colloidal gold, adsorbed on a carbon paste electrode, upon silver electrodeposition. A linear relationship was found between the area of the anodic stripping peak and the number of colloidal gold particles cm^{-3} and the detection limit of 1.25×10^7 gold particles cm^{-3} was obtained [5]. The anion exchange of tetrachloroaurates on a monmorillonite modified carbon paste electrode was studied in relation to a distribution of gold(III) complexes under the conditions used. A method for the determination of gold in aqueous solutions was investigated for the determination of gold in blood serum [6]. The anodic stripping determination of gold using a modified carbon paste electrode was investigated using preelectrolysis and the performance characteristics were estimated [7].

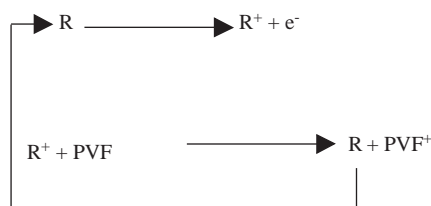
A glassy carbon electrode modified with poly(4-vinylpyridine) was used for the cathodic stripping voltammetric analysis of Au(III) in the presence of Cu(II) in a solution containing chloride or cyanide. The preconcentration in this modified surface was achieved through anion exchange of the complex ions of gold. The presence of Cu(II) caused some interference in chloride medium. A significant degree of interference was observed in cyanide medium [8]. Gold ions were preconcentrated on a glassy carbon electrode in media containing chloride and cyanide by electroreduction and analyzed by anodic stripping [9]. Interfering ions were removed by solvent extraction prior to analysis in later studies.

Metal surfaces that are coated with polymeric films are novel examples of chemically modified electrodes that offer new possibilities in electroanalysis [10]. Surfaces modified with redox polymers that contain ferrocene groups can be used as chemically modified electrodes [11]. Polyvinylferrocene (PVF) dissolved in methylene chloride can easily be converted to polyvinylferrocenium (PVF^+A^-) by electrooxidative precipitation at +0.70 V vs. Ag/AgCl. PVF^+A^- is insoluble in most solvents and so that electrode can easily be coated with this polymer in methylene chloride. The polymer that coats the surface contains ferrocene and ferrocenium groups and is electroactive itself. The conductivity of this material is due to the hopping of the electrons between this redox pair and increases with the degree of anion doping (A^-). The voltammetric anodic and cathodic peaks of the polymer appear at around +0.400 V vs. Ag/AgCl. The intensities of the peak currents vary with the type of solvent and the anion of the supporting electrolyte. Similar voltammetry peaks can also be observed when the electrode surface is coated with PVF by immersion in PVF solution and evaporation of the solvent. Electrooxidation and electroreduction of other depolarizers can also take place as a result of diffusion through the polymeric film and subsequent charge transfer at the electrode surface underneath.

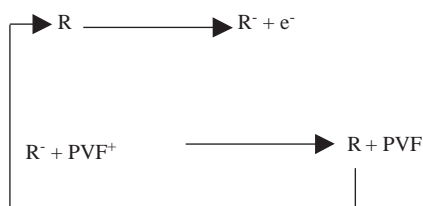
Various anions such as iodide, thiocyanate and cyanide can be incorporated and concentrated in the

PVF⁺A⁻ matrix via anion exchange. The electroactivity of the film arising from the ferrocenium/ferrocene redox couple either decreases or vanishes depending upon the type and concentration of the exchanging anion. The analysis of these anions can be accomplished by anodic stripping voltammetry after such a preconcentration step [12]. Depending upon the thickness of the film and the immersion time during the anion exchange type preconcentration step, electroactive anions with concentrations as low as 10⁻¹⁰ M can be determined by differential pulse anodic stripping voltammetry.

It was observed that the ferrocenium and ferrocene groups in the structure of PVF⁺A⁻ can also act as redox mediators. The electrooxidation of anthracene moiety (R) can be catalyzed by PVF sites in the polymer according to the following reaction, which regenerates neutral anthracene [13]:



Electroreduction of anthracene moiety, on the other hand, can be catalyzed by PVF⁺ sites in the polymer as follows, in which neutral anthracene is regenerated [14]:



This study aimed to develop a simple and reliable electrochemical method for the determination of gold.

A glassy carbon electrode modified with polyvinylferrocene was used in this study for the determination of gold ions, which are present as AuCl₄⁻ and AuBr₄⁻ in aqueous solution containing 1.0 M NaCl. Anodic stripping voltammetry allowed the determination of gold ions after a chemical preconcentration step.

Experimental

Polyvinylferrocene (PVF) was prepared by chemical polymerization of its monomer, vinylferrocene, at 70 °C [15]. The glassy carbon electrode was immersed in a solution of PVF in methylene chloride for a certain time period and the solvent was then evaporated. The surface was rinsed with triple distilled water before use. A yellow PVF film was coated on the glassy carbon surface after this procedure. The average thickness of the dry film was estimated from the charge, Q, consumed during complete electrooxidation of the film by stepping the potential from 0.0 to +0.70 V vs. SCE in 1.0 M NaCl solution as described by Bard [16].

All electrochemical measurements were carried out in an oxygen-free nitrogen (99.99%) atmosphere. All chemicals used were of analytical reagent grade. NaCl (Merck) was used to prepare the supporting electrolyte, and 10.00 mM KAuCl₄ (Merck), 10.00 mM KAuBr₄ (Merck) and 10.00 mM KAu(CN)₂ (Aldrich)

solutions were prepared as stock solutions. Solutions of lower concentrations were prepared by the dilution of the corresponding stock solution.

Electrochemical cell was a 3 electrode type with separate compartments for the reference and counter electrodes. A Pt foil with an area of 0.5 cm^2 was used as the counter electrode. The area of the glassy carbon working electrode was 0.0314 cm^2 (CH Instrument). SCE was used as the reference electrode.

An EGG-PAR Model 362 potentiostat together with a Linseis LY 16100-II X-Y recorder was used for electrochemical measurements.

Results and Discussion

Electrochemical behavior of AuX_4^- on PVF modified electrode

The cyclic voltammogram in Figure 1 is characteristic for a PVF coated glassy carbon electrode in 0.1 M NaCl solution. In the first cycle, the oxidation peak of PVF appears at about +0.55 V (vs. SCE), which shifts towards negative potentials during successive following cycles, corresponding to a reverse reduction peak of PVF^+ with a peak potential of +0.32 V vs. SCE. The cathodic peak was broader and less intense

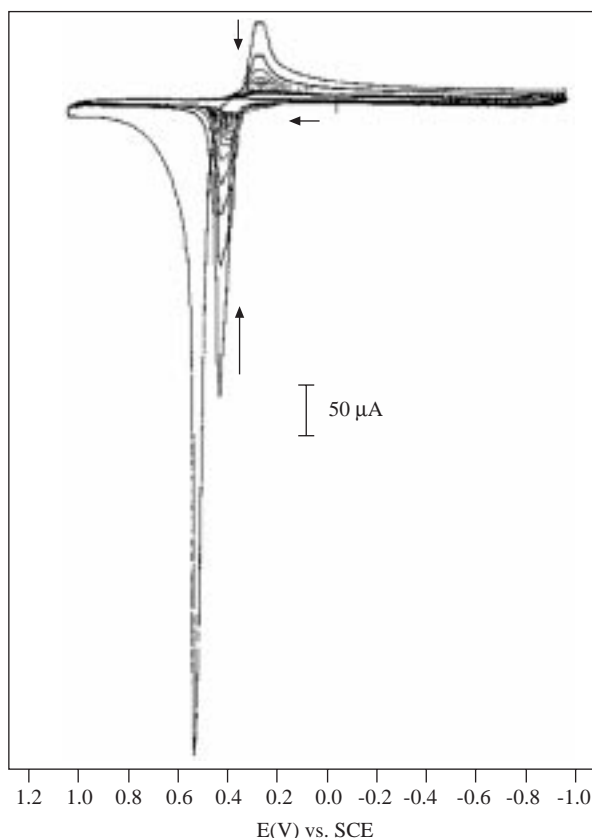


Figure 1. Multisweep cyclic voltammogram of $5 \times 10^{-8} \text{ mol cm}^{-2}$ of PVF (dry thickness $\sim 0.1 \mu\text{m}$) coated glassy carbon electrode in 1.0 M NaCl solution (sweep rate: 100 mV/s) “Vertical arrows indicate that the current values decrease during each successive scan. Horizontal arrow indicates the direction of the initial scan”.

than the anodic peak. Both peak currents decreased gradually and almost vanished during successive scans. Neutral PVF polymer takes counter ions into its structure when oxidized and swells. Deswelling occurs upon the reduction of the oxidized polymer as the counter ions are expelled from the structure. Swelling and deswelling kinetics of the polymer are not identical, which is the main reason for asymmetry of the anodic and cathodic peaks as was observed by other researchers [17].

The cyclic voltammogram of 2.0 mM KAuCl_4 solution on a glassy carbon electrode exhibited a broad and ill-defined reduction peak at +0.46 V vs. SCE on the forward scan and an oxidation peak at +0.94 V vs. SCE on the reverse scan (Figure 2). The oxidation peak appeared only after the potential was scanned first to the values beyond the reduction peak. The oxidation peak current increased and the color of the glassy carbon surface turned to yellow when the potential was held constant at these potentials. No oxidation peak was observed when the potential was first scanned anodically starting from +0.70 V vs. SCE. Similar cyclic voltammetry results were obtained for a solution of 2.0 mM KAuBr_4 solution on a glassy carbon electrode.

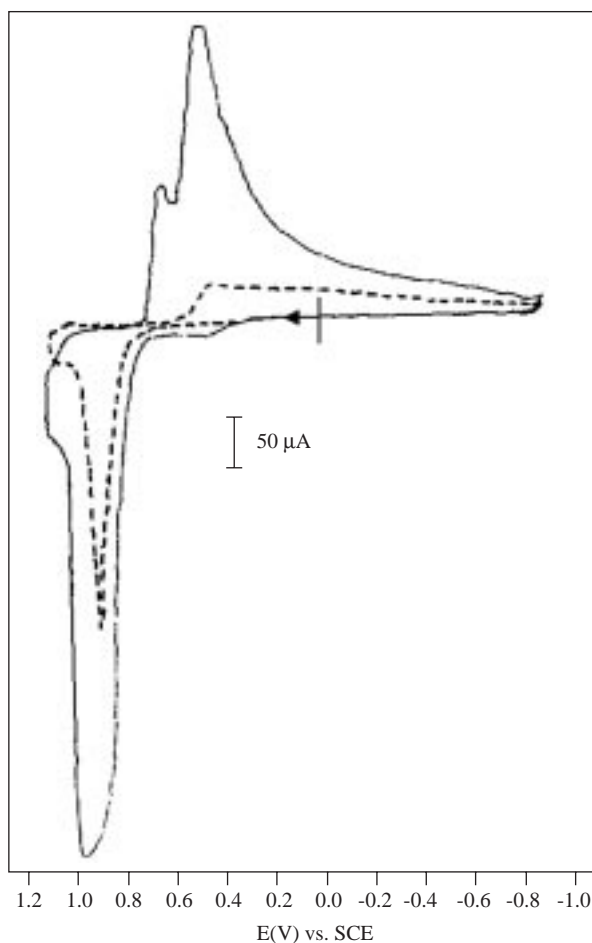
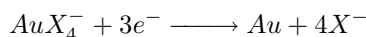
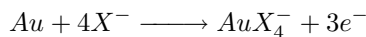


Figure 2. Cyclic voltammogram of 2.0 mM KAuCl_4 in 1.0 M NaCl solution on a uncoated glassy carbon electrode (---) and on a $5 \times 10^{-8} \text{ mol cm}^{-2}$ of PVF (dry thickness $\sim 0.1 \mu\text{m}$) coated glassy carbon electrode (—). sweep rate: 100 mV/s. “Horizontal arrow indicates the direction of the initial scan”.

These findings indicate that AuCl_4^- or AuBr_4^- is reduced to metallic gold during the cathodic forward scan:



and the metallic gold is oxidized during the reverse anodic scan:

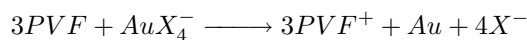


After the steady state was reached on the PVF coated glassy carbon electrode at the end of the successive potential scans, 2.0 mM $AuCl_4^-$ was added to the medium and the resulting cyclic voltammogram was reexamined. The reduction peak of $AuCl_4^-$ and the oxidation peak of Au were observed in the cyclic voltammogram (Figure 2). As seen in these voltammograms the oxidation peak current on the PVF coated glassy carbon surface was higher than that on the uncoated glassy carbon electrode.

AuX_4^- response of the PVF modified electrode

When the PVF coated glassy carbon electrodes were immersed in AuX_4^- solution for some time without the application of any potential, the gold oxidation peak was observed on the cyclic voltammogram of the film, which simultaneously changed color from yellow to green.

The accumulation of metallic gold on the PVF coated glassy carbon surfaces during immersion into AuX_4^- solution without the need for any electrolysis at cathodic potentials implies immediately that a chemical reduction takes place according to the following reaction:



As reported in our earlier studies [14], the PVF^+ film is green and the PVF film is yellow. The green film is soluble in dimethylformamide (DMF) and insoluble in methylene chloride. In contrast, the yellow film is soluble in methylene chloride and insoluble in DMF. Immersion of the PVF film in an aqueous solution containing 1.0 mM AuX_4^- for 5 min causes a change in the color of the film from yellow to green. The resulting film is insoluble in methylene chloride and soluble in DMF. This result provides independent chemical evidence for the occurrence of the redox reaction between PVF and Au(III).

Additionally, the cyclic voltammetry behavior of 2.0 mM dicyanoaurate(I) in an aqueous solution containing 1.0 M NaCl on glassy carbon electrodes was also investigated. It was found that the reduction peak potential of dicyanoaurate(I) is -1.36 V vs. SCE. When the PVF coated glassy carbon electrode was immersed in 1.0 mM dicyanoaurate(I) solution for a given time without the application of any potential, no gold oxidation peak was found on the cyclic voltammogram of the film. Interestingly, the cyclic voltammetry of the film that was immersed in the AuX_4^- solution showed the oxidation peak of the gold. The above results related to the electrochemical behavior of the PVF films can be interpreted in the following manner. The chemical redox reaction between PVF and AuX_4^- can take place easily in contrast to the reaction between PVF and $Au(CN)_2^-$ due to the oxidation potential of PVF and the reduction potentials of AuX_4^- and $Au(CN)_2^-$.

This observation provided an alternative possibility to preconcentrate Au^{3+} on the PVF coated glassy carbon surface in chloride or bromide containing aqueous medium prior to anodic stripping of the gold from this surface.

For AuX_4^- solutions of lower concentrations the anodic stripping peak of metallic gold at +0.94 V vs. SCE and the oxidation peak of PVF at +0.48 V vs. SCE were both observable in the cyclic voltammogram (Figure 3). For higher AuX_4^- concentrations, however, the PVF oxidation peak current decreased and the gold oxidation peak current increased substantially in the voltammogram (Figure 4). As outlined above, the PVF sites in the polymer matrix are oxidized by the chemical redox reaction between PVF and Au(III) causing a decrease in the oxidation peak current and an increase in the reduction peak current of the polymer.

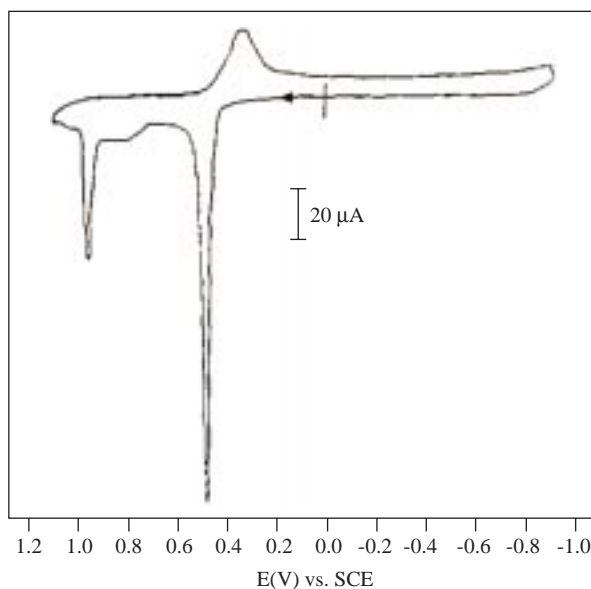


Figure 3. Cyclic voltammogram of a $5 \times 10^{-8} \text{ mol cm}^{-2}$ of PVF (dry thickness $\sim 0.1 \mu\text{m}$) coated glassy carbon electrode in 1.0 M NaCl solution after 5 min of immersion in 0.125 mM AuCl_4^- solution (sweep rate 100 mV/s). “Horizontal arrow indicates the direction of the initial scan”.

The effect of the thickness of the polymeric film

The effect of the thickness of the polymeric film was examined. The PVF coated glassy carbon electrodes were kept in 500 μL of the AuX_4^- solutions without stirring and the films were investigated by the anodic stripping voltammetry. When the aurate(III) ion concentration (1.0 mM) and plating time (5 min) were kept constant the thickness of the PVF film varied between $3 \times 10^{-8} \text{ mol cm}^{-2}$ of PVF (dry thickness $\sim 0.065 \mu\text{m}$) and $2 \times 10^{-7} \text{ mol cm}^{-2}$ of PVF (dry thickness $\sim 0.4 \mu\text{m}$). The gold oxidation peak current values increased with polymer thickness up to a value corresponding to $5 \times 10^{-8} \text{ mol cm}^{-2}$ of PVF (dry thickness $\sim 0.1 \mu\text{m}$), after which it remained constant. The average thickness of the PVF films was kept constant ($5 \times 10^{-8} \text{ mol cm}^{-2}$ of PVF) for all measurements.

The effect of accumulation time

It should be mentioned that it is important to choose an accumulation time when stripping studies are undertaken. The accumulation time dependence of the peak current resulting from Au incorporated in PVF film was examined and the results are shown in Figure 5. The concentration of aurate(III) ions in the solution

was 1.0 mM in this study. The thickness of the PVF film was 5×10^{-8} mol cm^{-2} of PVF, corresponding to $\sim 0.1 \mu\text{m}$ dry thickness. The anodic stripping peak current of metallic gold increased sharply at a short plating time and then increased gradually, finally approaching a saturation value after 5 min. All of the measurements were carried out using this immersion time.

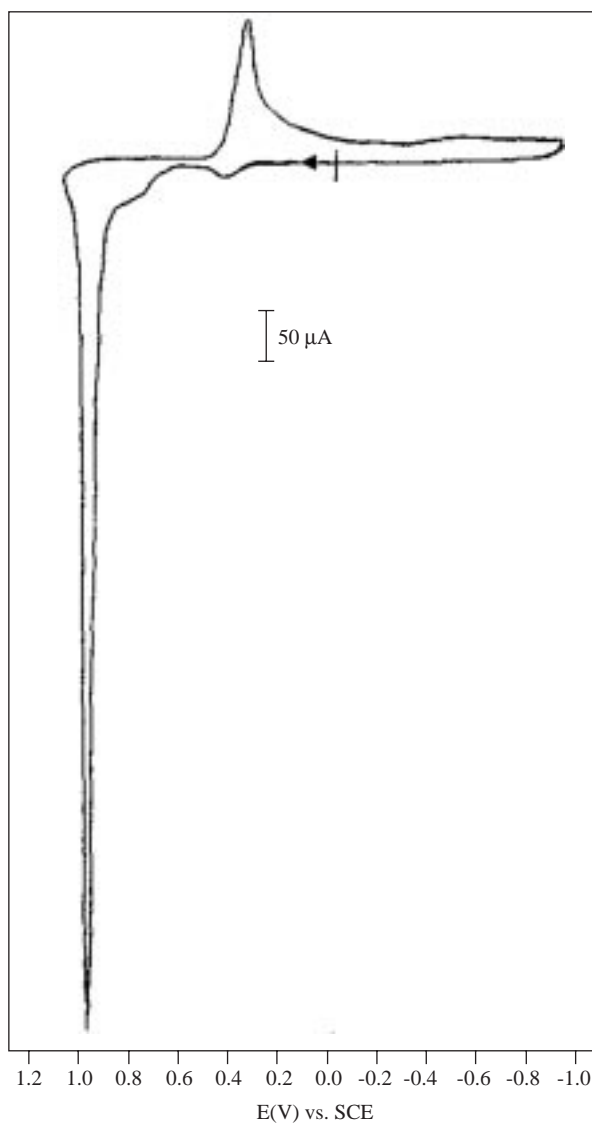


Figure 4. Cyclic voltammogram of a 5×10^{-8} mol cm^{-2} of PVF (dry thickness $\sim 0.1 \mu\text{m}$) coated glassy carbon electrode in 1.0 M NaCl solution after 5 min of immersion in 0.850 mM AuCl_4^- solution (sweep rate, 100 mV/s). “Horizontal arrow indicates the direction of the initial scan”.

The constant current observed at higher accumulation times results because of the limiting number of PVF centers, which determines the amount of gold accumulation at the surface.

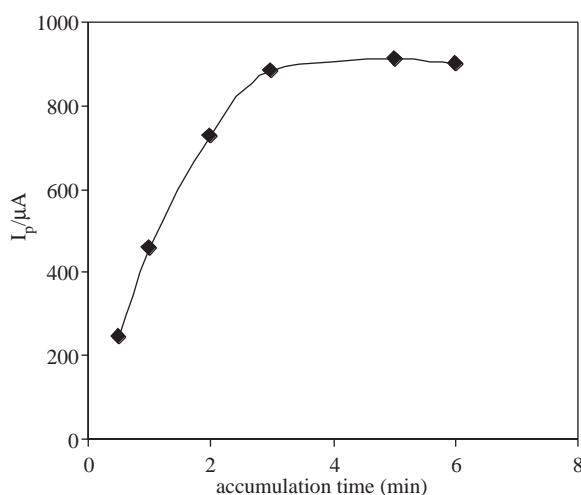


Figure 5. The effect of the duration of immersion of a 5×10^{-8} mol cm^{-2} of PVF (dry thickness $\sim 0.1 \mu\text{m}$) coated glassy carbon electrode in 1.0 mM AuCl_4^- solution on the anodic stripping peak current of gold.

Analytical characterization

Figure 6 shows the effect of the concentration of AuX_4^- solution on the measured anodic stripping peak current after 5 min of preconcentration. The data points in Figure 6 are the averages of 3 measurements. The relative standard deviations for measurements taken to construct the calibration plots in Figure 6 were calculated. Except for one set of measurements for the samples of the lowest concentration (0.125 mM) the relative standard deviations were equal to or less than 3%. The relative standard deviation for 0.125 mM was 7%. The calibration plots constructed under these conditions gave linear working ranges up to a value of 0.850 mM of AuX_4^- concentration. The minimum AuX_4^- concentrations that produced detectable peak currents were 0.125 mM. The linear correlation coefficients of the calibration curves were better than 0.99. Both values indicate that the precision of the method is quite satisfactory. For immersion times of 5 min in AuX_4^- solutions more dilute than 0.125 mM, no anodic stripping peak for gold was measurable. It was therefore necessary to increase the preconcentration times for such dilute solutions. With an immersion time of 60 min, for example, an anodic stripping peak for AuX_4^- concentrations as low as 0.0156 mM was detectable.

Anodic stripping voltammetry is a low-cost, sensitive and simple method. However, problems arise with the use of anodic stripping voltammetry for gold determination in the presence of copper. The tendency of gold and copper to form an amalgam during the electrodeposition step leads to erroneously high analytical results. Therefore, the effect of Cu^{2+} ions was investigated. Various amounts of Cu^{2+} ions were added to a solution containing 0.900 mM AuCl_4^- in order to determine the interference effect. As seen in Table, the anodic stripping peak current value of gold was not affected by the presence of Cu^{2+} ions up to a concentration value 20 times greater than that of AuCl_4^- ions.

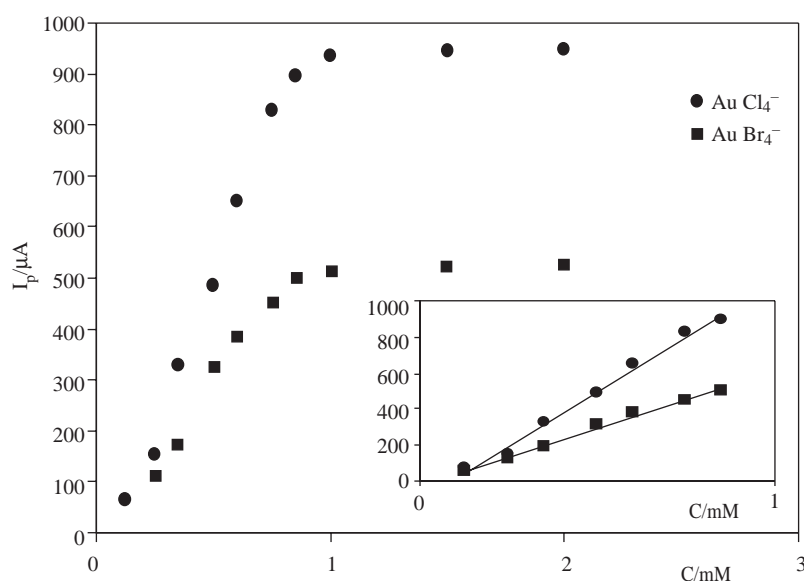


Figure 6. The effect of the concentration of AuCl₄⁻ and AuBr₄⁻ solutions during immersion on the anodic stripping peak current of gold after 5 min of immersion with a 5×10^{-8} mol cm⁻² of PVF (dry thickness $\sim 0.1 \mu\text{m}$) coated glassy carbon electrode.

Table. Interference of Cu²⁺ ions with 5 min preconcentration time (AuCl₄⁻ concentrations are 0.900 mM).

CuCl ₂ Concentration (mM)	Percent change in the stripping peak current of gold
0.10	not detected
1.0	not detected
10	not detected
20	not detected
50	-5.39
100	-17.59

Conclusion

The anodic stripping determination method of gold described in this study provides an alternative procedure to the existing works proposed in the literature in the preconcentration step [1-9]. Metallic gold can be easily incorporated and concentrated in the PVF coated glassy carbon electrode by means of the chemical reduction of AuCl₄⁻ and AuBr₄⁻ ions by PVF. It can then be stripped off the surface anodically without any need for preelectrolysis at cathodic applied potentials. If gold cyanide complex ions are used instead of the chloride or bromide complex, a reductive electrolysis prior to the anodic stripping is needed since the reduction of the cyano complex occurs beyond -1.36 V vs. SCE whereby inhibiting the chemical reduction by PVF. Pre-electrolysis is applied in other studies for the deposition of gold. The detection limit was to found to be 5 $\mu\text{g/L}$ by Lintern and 10 ppb by Jacobs. The detection limit was 1.56×10^{-6} M in this study. Although the detection limit is greater than those measured in other studies the electrode coating and gold deposition procedures are much simpler than those in these 2 studies. The standard deviation in this work is about 3 %,

which is much better than those found in these other 2 studies (5 % and 10 %, respectively). Furthermore, interference by copper ions is minimal in our work.

The electrode surface coated with PVF layer thus offers some novel application possibilities in the field of chemically modified electrodes. In this study, an advantageous procedure was developed, allowing the preparation of gold deposited modified electrodes since metal deposited modified electrodes have been recently recognized to have potential applications in electrocatalysis and electroanalysis.

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