

STRIPPING VOLTAMMETRY USING MERCURY MICROELECTRODES FOR MULTI-ELEMENT DETERMINATION

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SUMMARY

Mercury film microelectrodes, prepared by potentiostatic electrodeposition of Hg(II) from an acidic solution onto a gold microdisk electrode, in combination with adsorptive stripping voltammetry in the presence of catechol were used to study the behavior of copper, iron and nickel in aqueous solutions. The voltammetric behavior of hydrogen ion was also investigated by performing cyclic voltammetry and stripping voltammetry with mercury microelectrodes.

INTRODUCTION

Mercury has been widely used as an electrode material in voltammetric techniques to determine metal ions concentrations and speciation in water samples [1-3]. For these studies, stripping voltammetry is an advantageous technique due to its rapid accumulation of the metal-ligand at the surface. Such procedure was applied to determine iron [4], cobalt [5], nickel [3], selenium [6], and copper [7]. The mostly used ligands are dimethylglyoxime, di-o-hydroxyazo dyes, catechol and oxine which are considered as adsorption enhancement reagents.

Microelectrodes made of metal wires such as carbon, platinum or gold have shown to possess several unique advantages and applications over conventional electrodes. A

combination of these microelectrodes with a mercury film grown potentiostatically at the metal tip has broadened the scope of use in routine electroanalytical applications [8]. The mercury grown films are characterized for being stable, easy made, durable and reproducible. Furthermore, Wightman et al. [8] have claimed that they present a hemispherical geometry of known dimensions, and that they exhibit uniform accessibility for the diffusion of electroactive species to the interface.

Stripping voltammetry (SV) is a very sensitive electroanalytical technique for the trace analysis of metal ions with detection limits as low as 10^{-10} mol l⁻¹ to 10^{-12} mol l⁻¹ [9]. However, when conventional mercury electrodes are employed the concentration of the metal ion of interest at the surface is only achieved by inducing convection (e.g. mechanical stirring, use of a rotating disk, etc.) causing irreproducibility on the mass transport process which results in a source of error [10-11]. Wightman et al. [8] has reported that the use of mercury film microelectrodes do not require induced convection because of the enhanced mass transport by radial diffusion, eliminating this source of error in the SV technique.

In the field of biomaterials, mercury microelectrodes coupled with the adsorptive stripping technique have been used to determine metal ions released from metallic materials (e.g. stainless steel AISI 316L and titanium). We have previously demonstrated that mercury film microelectrodes allow to quantify iron [12] and nickel [13] trace levels in osteoblast-like cell culture medium when studying the mineralization process which occurs at the metallic biomaterials surface. Mercury film microelectrodes also facilitate the determination of nickel in mice organs such as liver, kidney and spleen when performing *in vivo* studies towards the understanding the effects caused by the biodegradation of these metallic implants [14-15]. Preliminary investigations of titanium quantification in mice organs using similar procedures are being undertaken.

This paper reports a study carried out in aqueous media using the stripping voltammetry technique and mercury microelectrodes to illustrate their versatility in the electroanalytical domain. In a single measurement it is feasible to determine copper, iron and nickel with the aid of catechol as the surface active organic material. The optimal experimental parameters are discussed. pH was also targeted in this study. Possible interferences and detection limits are investigated.

EXPERIMENTAL

All reagents used were of analytical grade and deionized and triply distilled water was used for preparing all solutions. The mercury deposition solution was a deoxygenated solution containing 1.00 mol l⁻¹ KNO₃ plus 5.70×10^{-3} mol l⁻¹ Hg(NO₃)₂ and 0.50% concentrated nitric acid [16]. A buffer solution of 0.10 mol l⁻¹ PIPES (piperazine-N,N'-bis-2-ethane sulphonic acid) with a pH value of *ca.* 8.0 was prepared in 0.05 mol l⁻¹ NH₄OH. A stock solution of 0.10 mol l⁻¹ catechol was prepared daily and oxygen was removed immediately by purging with nitrogen to prevent the oxidation of catechol to the corresponding o-quinone [17].

An AUTOLAB potentiostat/galvanostat model PSTAT 10 coupled with an ECD Module from EcoChemie controlled by a PC, through the Model GPES3 software, was used for all electrochemical measurements. The electrochemical studies were performed with a working mercury microelectrode, an Ag/AgCl/3.00 mol l⁻¹ KCl reference electrode and a cylindrical carbon counter electrode. Electrical connections were made with low noise coaxial cables and the electrochemical system was placed inside a thick-walled aluminum Faraday cage to avoid external interferences. pH measurements were made with a Metrohm AG CH-9100 Herisau pH meter.

The electrochemical studies of copper, iron and nickel in aqueous media were performed by square wave voltammetry. The solution was pipetted into a polarographic cell and the pH was adjusted to 7.9-8.1 by addition of 0.10 mol l⁻¹ PIPES buffer. The solution was deoxygenated by purging with nitrogen during a period of 15 min. and then catechol was added. The final concentration in the sample of the buffer and of the complexing agent were 1.00×10^{-2} mol l⁻¹ and 5.00×10^{-4} mol l⁻¹, respectively.

The voltammetric behavior of hydrogen ion in aqueous solutions was investigated using cyclic voltammetry and square wave voltammetry and no complexing agent or buffer was used. In all solutions the pH was adjusted with diluted nitric acid.

All the experiments were performed using a working mercury microelectrode. Before each experiment, a gold microdisk electrode with a diameter of 25 μm was polished with 1.50×10^{-2} μm alumina until a perfect cyclic steady-state voltammogram was obtained in a solution containing 0.10 mol l⁻¹ of iron (III)/iron (II) in 1.00 mol l⁻¹ of

KNO₃ aqueous solution. The mercury microelectrode was prepared by electrodeposition of mercury onto the gold electrode by the application of a constant potential of 0.00 V (vs. Ag/AgCl) [16] during a deposition time of 60 s. The working mercury microelectrode was then rinsed with distilled deionized water and inserted in the solution to be analyzed. The growth of the mercury films was monitored by the chronoamperometry technique.

RESULTS AND DISCUSSION

Trace levels detection of copper (Cu), iron (Fe) and nickel (Ni) using the same ligand (e.g. catechol) has been achieved by using mercury film microelectrodes. In order to obtain a well-defined peak separation for each metal ion, especially between iron and copper, the working parameters with major influence on the resolution of adjacent peaks were optimized, namely potential of adsorption, amplitude and pH. For the lowest value of potential adsorption applied (-0.05 V), Cu is the species highly reduced at the surface of the microelectrode as illustrated in Fig. 1A. As the potential of adsorption increases the resolution becomes more clarified being possible to obtain a compromise between Cu and Fe peaks (Fig. 1B). Increasing negatively the potential of adsorption, Fe is preferentially reduced at the surface (Fig. 1C). From this figure it is clear the importance played by the potential of adsorption for multi-element quantification by performing adsorptive stripping voltammetry.

From the voltammograms represented in Fig. 1, one can predict that depending on the potential of adsorption applied, specific quantification of a certain metal ion can be achieved. These expectations only hold for mercury electrodes. Apparently, metal-catechol complex ions are adsorbed onto the mercury surface, giving rise to a large reduction peak when the potential is swept to more negative values. This peak is not caused by the reduction of catechol but by that of metal ion, as the peak height is directly proportional to the metal concentration and the reduction potentials correspond to those for copper and iron. When the potential of adsorption is greatly increased to more negative values, say to -1.80 V, and the potential is scanned from less negative values to more negative values, improved sensitivity and well defined peaks related to

the reduction of adsorbed complex ions of copper at -0.20 V, iron at -0.35 V and nickel at -0.95 V are measured as illustrated in Fig. 2. Considering that a deposition potential of -1.80 V is used (anodic stripping voltammetry) and the signal of the current observed is negative which corresponds to a reduction phenomenon (cathodic stripping voltammetry) it may seem that data are contradictory. The same pattern of behavior was already observed by Capodaglio et al. [18] in the determination of antimony in sea water using catechol as the complexing agent. The accumulation process of Cu, Fe and Ni changed from a simple adsorption at deposition potentials more positive than *ca.* -0.20V for Cu, *ca.* -0.35 V for Fe and *ca.* -0.95 V for Ni (which correspond to the peak potentials for the Cu-, Fe- and Ni-catechol complexes) to amalgamation followed by adsorption when a potential of -1.80 V is used. The amalgamated Cu, Fe and Ni are re-oxidized to Cu²⁺, Fe³⁺ and Ni²⁺, complexed by catechol, and subsequently re-adsorbed when the potential is set to -0.10 V (or -0.05 V) to begin the scan. So, re-adsorption occurred only during the period between switching to the scan start potential, -0.10 V or -0.05 V, and scanning until the reduction potential of the ions had been reached [12]. The use of -1.80 V as the optimum adsorption potential and consequently, limiting the re-adsorption step to the time of scanning, allows to achieve maximum peak separation between copper and iron.

The influence of the amplitude on the peak height and on the resolution of adjacent peaks was studied by ranging the amplitude from 2.5 mV to 100 mV. A linear relation between the peak current and the amplitude was observed up to 20 mV. Larger square wave amplitudes provide greater sensitivity [19] at the expense of overlapping of the copper and iron peaks. An amplitude value of 20 mV was considered the most appropriate, being a compromise between sensitivity and resolution of adjacent peaks.

The effect of pH on peak height and on peak separation was also studied. As the pH of the solution decreases, the iron peak moves closer to that of the copper and interference occurs [20]. At pH 7.0, van den Berg and Huang [21] found necessary to mask the copper with EDTA for iron determination. Bearing in mind that optimum sensitivity for copper and iron lies in the range of pH 7.8-8.5 [17] and that good separation between peaks is achieved for higher pH values, a working pH value of *ca.* 8.0 was selected.

The application of adsorptive stripping voltammetry to the analysis of samples containing these metal ions using mercury film microelectrodes is a reliable procedure. The voltammogram represented in Fig. 2 points out to the fact that catechol is not a specific chelator of a metal ion but, at most, is selective to metal ions. However its sensitivity (peak/concentration) for copper is higher than for the other metal ions present in the samples.

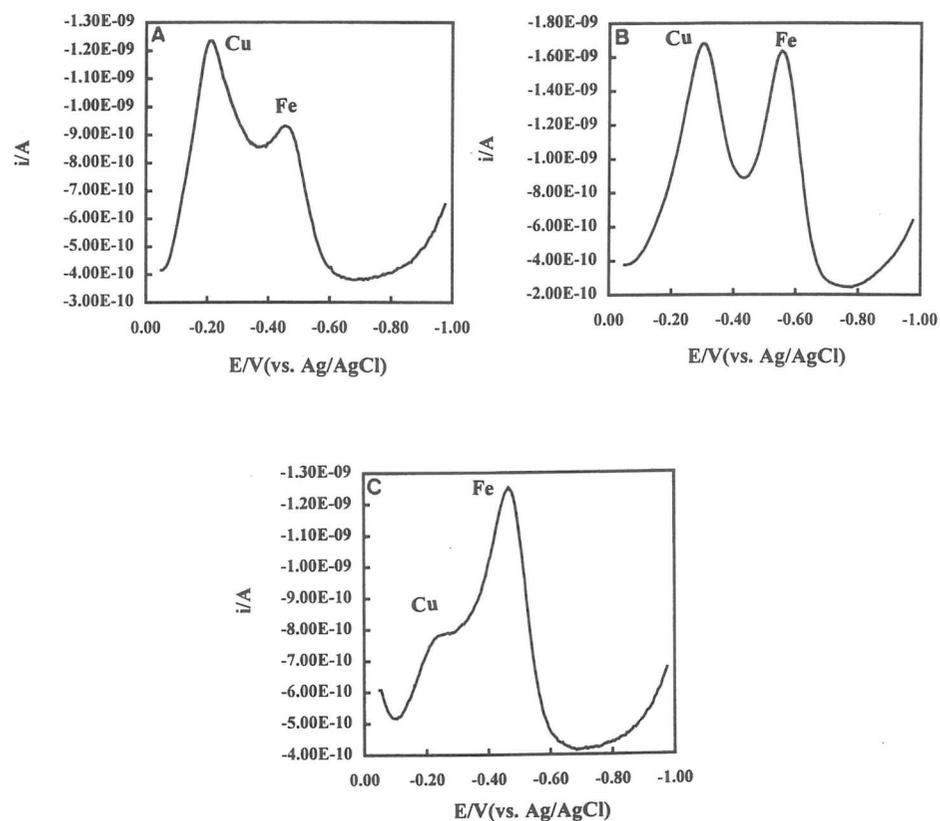


Figure 1- Voltammograms showing the influence of adsorption potential on the resolution of the copper and iron peaks: (A) adsorption potential=-0.05 V; (B) adsorption potential=-0.20 V; (C) adsorption potential=-0.25 V.

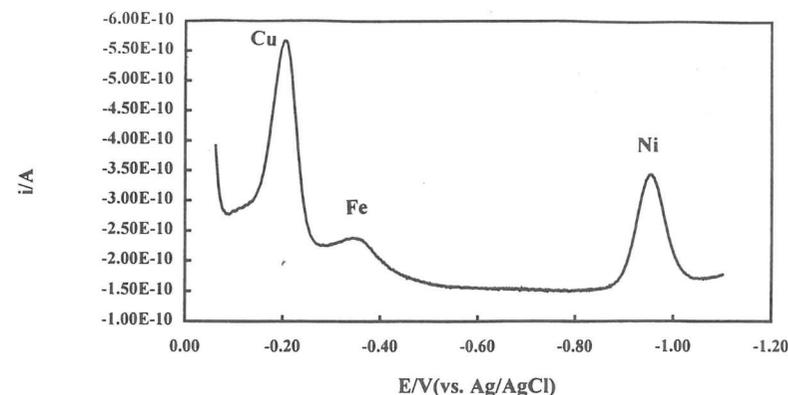


Figure 2- Voltammogram obtained for a value of adsorption potential of -1.80 V showing perfect separation between copper (-0.20 V), iron (-0.35 V) and nickel (-0.95 V) peaks.

The voltammetric behavior of hydrogen ion in aqueous solutions using mercury microelectrodes was also studied. Two electrochemical techniques were used, namely cyclic voltammetry and cathodic stripping voltammetry and the preconcentration was carried at -0.90 V as it yields a maximum hydrogen peak height. As it can be observed in Fig. 3, the reduction peak of hydrogen appears around -1.52 V and it is only detectable for concentrations higher than *ca.* $1.00 \times 10^{-3.5}$ mol l⁻¹ which corresponds to the practical limit of detection. Two calibration curves obtained by the standard additions method are presented in Fig. 4 and Fig. 5 showing that the reduction peak of hydrogen is so intense that even a less sensitive techniques such as cyclic voltammetry can be used for pH determination by using mercury microelectrodes.

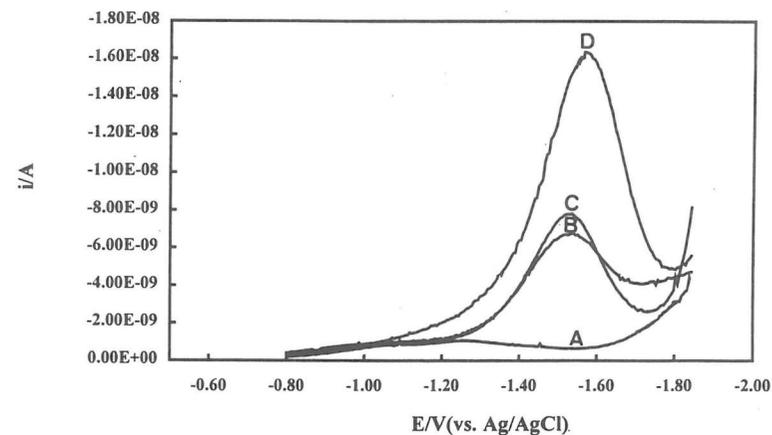


Figure 3- Voltammograms showing the increase of hydrogen peak with the decrease of pH value: (A) pH=3.70; (B) pH=3.28; (C) pH=3.05; (D) pH=2.84.

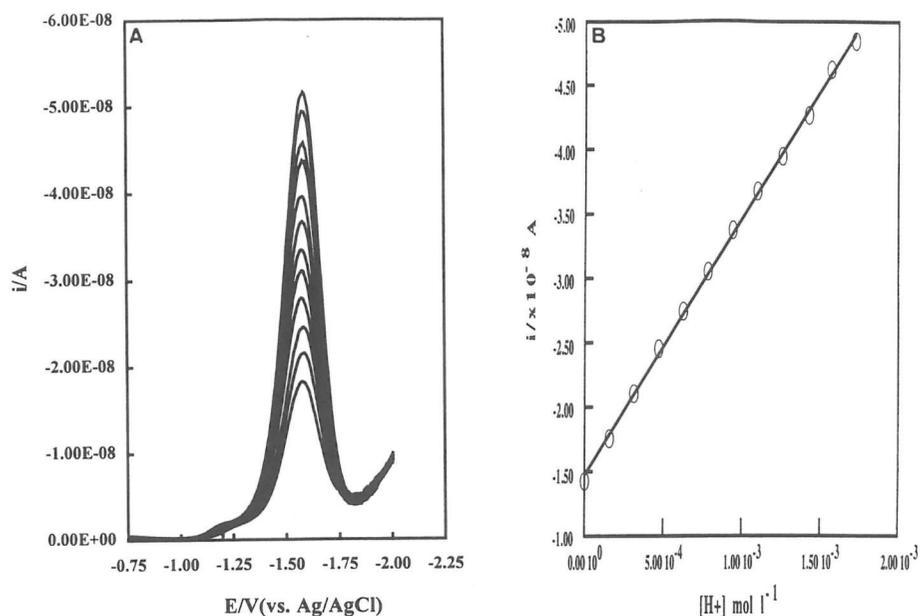


Figure 4- Determination of hydrogen concentration in an aqueous solution by square wave voltammetry: (A) stripping voltammograms; (B) calibration curve obtained by the standard additions method.

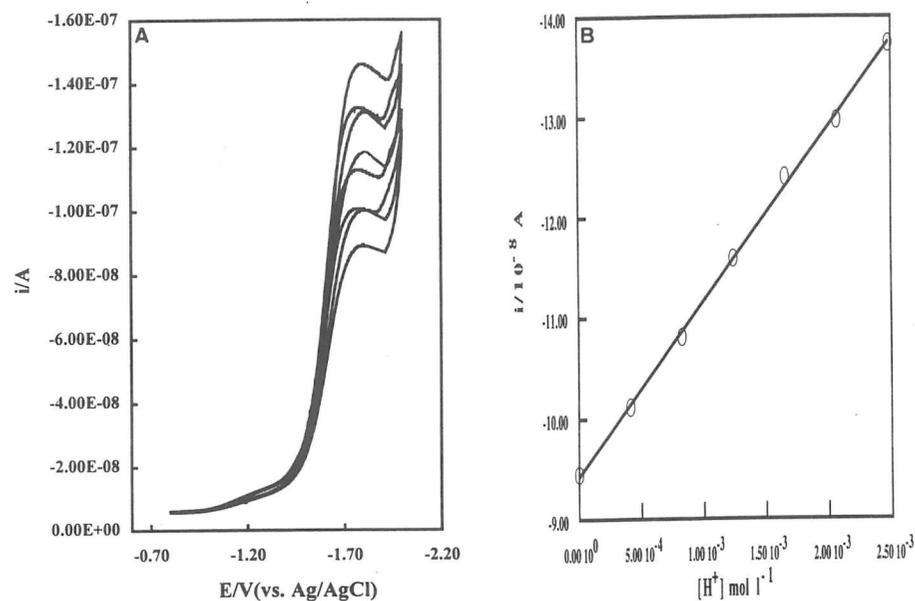


Figure 5- Determination of hydrogen concentration in an aqueous solution by cyclic voltammetry: (A) cyclic voltammograms (only some voltammograms are represented to facilitate figure's understanding); (B) calibration curve obtained by the standard additions method.

The cyclic voltammograms represented in Fig. 5 indicate, also, that the diffusion current assumes a steady-state value since a plateau is observed in the i - E curve and that the limiting diffusion current is directly proportional to the surface concentration of hydrogen ion. The occurrence of the plateau corresponds to the diffusion of H^+ species through the mercury. After completion of the diffusion process, the current starts to increase drastically due to hydrogen evolution.

CONCLUSIONS

This work has emphasized that multi-element determination is possible when using mercury microelectrodes in combination with the adsorptive stripping technique. The presence of a complexing agent selective for the metal ions targeted is obviously necessary and an exhaustive study of all the working parameters is essential in order to obtain optimal sensitivity and maximum peak separation between adjacent peaks.

Also, it was observed that mercury microelectrodes can be used as sensors of hydrogen ion in acidic solutions.

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p-Substituted Benzoic Acid Derivatives as Corrosion Inhibitors for Aluminium in H₃PO₄

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ABSTRACT

The use of some p-substituted benzoic acid derivatives as low cost inhibitors for the corrosion of aluminium in 60% H₃PO₄ solution was explored by weight loss and galvanostatic polarization measurements. The inhibition efficiency of the compounds increases in the order: p-OH > p-NH₂ > benzoic acid > p-Br > p-NO₂. This order is not affected by the variation in temperature in the range 30-60 °C. Rate of corrosion is affected by both concentration of inhibitors and the temperature of the medium. The reaction rate was found to be proportional to the absolute value of Hammett constant (σ). Some thermodynamic functions were computed and are discussed.

Key words: Corrosion, aluminium, polarization, weight-loss measurements.

INTRODUCTION