

SQUARE WAVE STRIPPING VOLTAMMETRY AT WALL-JET ELECTRODES

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ABSTRACT

Square wave stripping voltammetry at wall-jet mercury thin film electrodes in continuous flow has been investigated, with particular attention to the anodic stripping voltammetry of zinc, cadmium, lead and copper, and the adsorptive stripping voltammetry of cobalt and nickel via the formation of complexes with nioxime ligand. Advantages of square wave voltammetry with respect to differential pulse voltammetry in the determination step and to batch determination without continuous flow are demonstrated. Nanomolar detection limits are found. Optimisation of experimental procedures is discussed.

INTRODUCTION

Wall-jet electrodes have important applications in continuous flow systems for the monitoring of electroactive species [1], and can be used to advantage in diverse electroanalytical problems. On-line monitoring of trace metals is of great interest for environmental control, and for which wall-jet electrodes are especially appropriate given the ease with which they can be introduced at any point in a flow system through the introduction of appropriate branching manifolds.

Previous work has demonstrated the use of stripping voltammetric techniques at wall-jet mercury thin film electrodes - anodic and adsorptive stripping voltammetry (ASV and AdSV respectively), e.g. [2,3], - leading to practical detection limits in the nanomolar range. In most of these studies linear scan or differential pulse (DP) voltammetry was used in the determination step. Important advantages of square wave voltammetry in the determination step, apart from increased sensitivity, are first that it obviates the need for deoxygenation of the sample analyte solution and secondly that it reduces the timescale of the determination step from 1-2 minutes (DP) down to a few

seconds, thus increasing sample throughput. The square wave ASV of lead and cadmium at wall-jet electrodes was recently investigated by us [4] and its merits relative to differential pulse ASV at the wall-jet and at stationary electrodes in stirred solution demonstrated.

Square wave ASV at wall-jet electrodes has now been further studied to include copper and zinc and mixtures of all four elements. Square wave adsorptive stripping voltammetry of cobalt and nickel via the accumulation of nioxime complexes has also been carried out and compared with the previous procedure at wall-jet electrodes using differential pulse voltammetry in the determination step [3].

EXPERIMENTAL

A wall-jet cell was used as described previously [3,4], and contained a glassy carbon disc electrode, diameter 0.3cm, a platinum tube auxiliary electrode in the cell outlet and an Ag|AgCl (3.0M KCl) reference electrode. Experiments were controlled using an Eco-Chemie PSTAT10 Autolab. A peristaltic pump provided flow rates between 0.035 and 0.045 cm³ s⁻¹. Solutions were made from analytical grade reagents. All experiments were carried out at room temperature (22-23°C) without deoxygenation of the sample solutions.

RESULTS AND DISCUSSION

The results obtained for the anodic stripping and adsorptive stripping voltammetric procedures will be described separately and general merits referred to in the final remarks.

Anodic stripping voltammetry

Investigation showed that good results were obtained by the formation of mercury thin films by co-deposition of mercury with the metal from analyte solutions, containing zinc, cadmium, lead or copper ions or mixtures of these, spiked with 10⁻⁴M Hg²⁺ and in 0.1M sodium perchlorate electrolyte. Deposition potentials were either -1.0V vs. Ag|AgCl or -1.3V (for analysis of zinc), followed by a square wave scan in the determination step towards positive potentials to reoxidise the metal. Peaks for stripping of these elements from the mercury thin film appear at -1.14, -0.63, -0.55 and -0.05V respectively, and have the characteristic asymmetrical profile of a peak recorded under convective flow conditions. A typical variation of peak current with deposition time is shown in Fig.1 for cadmium and lead. Note the non-linearity at long deposition times; this results from limitations in forming thick mercury films and the low solubility of the

metals in mercury. Good linear calibration curves were obtained with practical detection limits in the nanomolar range. This is better than the equivalent procedure using differential pulse voltammetry or using square wave voltammetry at stationary electrodes in stirred solution [4].

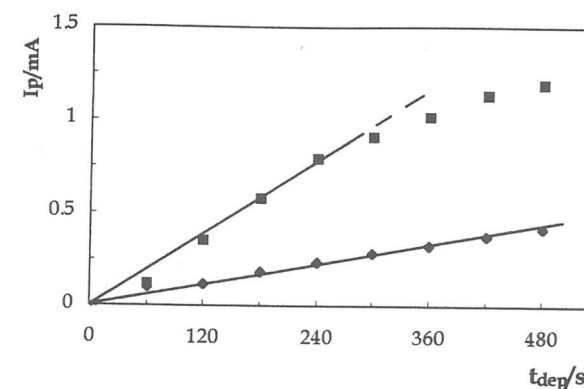


Fig.1 Plot of peak current as a function of deposition time for SWASV of ■ cadmium ([Cd²⁺]=50nM) and ◆ lead ([Pb²⁺]=50nM) at the wall-jet electrode; $V_f=0.045\text{cm}^3\text{ s}^{-1}$. Square wave parameters: amplitude 50mV, frequency 100Hz, scan increment 2mV.

It was found that the effects of Zn-Cu intermetallic compound formation in mercury can be conveniently removed by addition of gallium ion to preferentially complex with Cu. Alternative procedures, used for differential pulse voltammetry, based on the difference between signals obtained from deposition of Cu without Zn at -1.0V and deposition of both at -1.3V did not give satisfactory, reproducible responses.

Adsorptive stripping voltammetry

In the case of adsorptive stripping voltammetry, it was necessary to form mercury thin films prior to determination by electrodeposition at -1.0V vs. Ag|AgCl under continuous flow conditions; this was done from a solution containing 10⁻⁴M Hg²⁺, 0.1M KNO₃ and 5mM HNO₃. The flow stream was then switched to the analyte solution, containing cobalt and/or nickel ions in supporting electrolyte of 30mM HEPES, 0.1M sodium perchlorate and 10⁻⁴M nioxime. The complexes were accumulated on the electrode surface at -0.7V vs. Ag|AgCl and the metal ion reduced in the determination step by a negative-going square wave voltammetric scan.

Typical results lead to peaks for nickel and cobalt at -0.94V and -1.01V ($f=100\text{Hz}$) with an asymmetric hydrodynamic profile; peak positions change with square

wave frequency but peak separation is constant and independent of frequency. Saturation of the electrode surface is evident at long adsorption accumulation times, Fig.2, as it was for differential pulse AdSV [3].

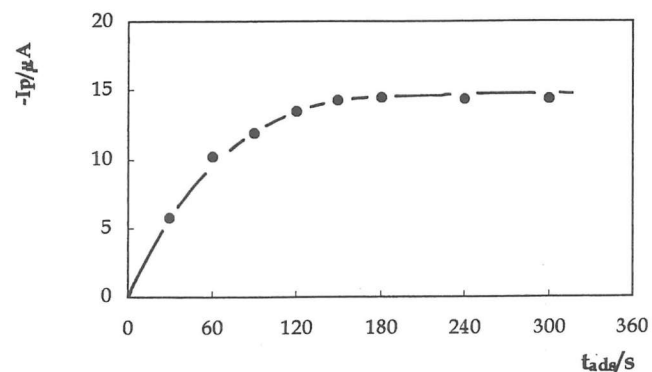


Fig.2 SWAdSV of cobalt: variation of peak current for reduction of adsorbed cobalt-nioxime complex with adsorption time, t_{ads} ; $[Co^{2+}] = 8nM$. Square wave parameters: amplitude 30mV, frequency 100Hz, scan increment 2mV.

Calibration curves have slopes of $0.7\mu A/nM$ for nickel and $1.3\mu A/nM$ for cobalt under optimised experimental conditions (compare $0.08\mu A/nM$ and $0.17\mu A/nM$ for DPAdSV [3]), which represents a sensitivity enhancement of an order of magnitude.

Final remarks

Square wave anodic and adsorptive stripping voltammetry at wall-jet mercury thin-film electrodes is shown to be successful and leads to the same nanomolar detection limits and similar sensitivities as compared to the differential pulse analogues. The particular advantages arise from the removal of the necessity for solution deoxygenation and the faster determination step which can usefully increase sample throughput. This is of importance in on-line monitoring applications.

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ELECTROCHEMICAL REDUCTION OF FLUOXETINE

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ABSTRACT

The electrochemical reduction of fluoxetine was studied using a hanging mercury drop electrode in different buffer solutions up to pH 13 and with concentrations of fluoxetine varying from $1.0 \times 10^{-6} M$ to $5.0 \times 10^{-5} M$. A very strong adsorption of fluoxetine on the electrode was observed and the shape of the cyclic voltammograms suggests that in these conditions it corresponds to a quasi-reversible system for adsorbed species. The results obtained for the electrochemical quantification of fluoxetine in five pharmacological formulations existing in the Portuguese market were compared.

INTRODUCTION

Fluoxetine is an anti-depressive used very successfully due to its small secondary effects, namely cardiovascular and colinergic. Its action is through inhibition of the uptake of serotonin by the neurons in the brain, consequently enhancing serotonin neurotransmission.

