

the use of microelectrodes allows the electrochemical determination of styrene in toluene containing a small percentage of DMF in order to dissolve the supporting electrolyte, and in a previous work<sup>4</sup>, a mixture of toluene / DMF (90/10) was used for the styrene determination using SWV and a gold microdisc of 6  $\mu\text{m}$  of radius. Also in this case the GLC analysis provides a value of styrene percentage which is in good agreement with that obtained by SWV.

The above results, seem to indicate that this method for styrene determination can be easily applied to other copolymers. Depending upon the solvent used for the polymer dissolution, micro or conventional sized electrodes may be used.

The electrochemical method offers several advantages over chromatography since it does not require sample preparation, it is quicker to register a voltammogram than a chromatogram and the equipment is cheaper.

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## BATCH INJECTION ANALYSIS WITH STRIPPING VOLTAMMETRY

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#### ABSTRACT

Batch injection analysis in conjunction with preconcentration by anodic stripping voltammetry and adsorptive stripping voltammetry has been investigated and optimised. Mercury films are pre-formed *in situ* within the cell on glassy carbon substrates by injection of 100 $\mu\text{l}$  electrolyte containing mercury ions. Increased electrolysis efficiency in the stripping experiment is obtained by continuing preconcentration after injection of  $\leq 100\mu\text{l}$  of the metal-ion-containing analyte. Detection limits are in the nanomolar range. This procedure should find widespread application to all types of stripping voltammetry.

#### INTRODUCTION

In batch injection analysis (BIA) a small sample of analyte (generally  $\leq 100\mu\text{l}$ ) is injected directly into an appropriate detection zone. The technique thus has characteristics of flow injection analysis (FIA) with very low dispersion and, during the injection period, of continuous flow analysis. Particular advantages can be gained by using motorised electronic micropipettes for the injection resulting in high accuracy and reproducibility, and the possibility of performing sequential injections at small time intervals.

For electrochemical amperometric and voltammetric detection, the sample is injected directly over the centre of a disc electrode immersed in electrolyte solution. The hydrodynamics during injection is thus of the wall-jet type which has been demonstrated [1], and which is almost without memory effects. Point-by point voltammetric curves can be registered from successive injections at different potentials, and cyclic and square wave voltammograms can be registered during injection enabling the determination of thermodynamic and kinetic parameters as well as of concentration from the same experiment [2].

For the determination of trace species by electrochemical methods, preconcentration on the electrode has to be employed. This approach at a mercury thin film electrode combined with BIA will be described for the measurement of trace metals by anodic stripping voltammetry (ASV) or adsorptive stripping voltammetry (AdSV). Merits arise from the low consumption of sample and the low contact time between sample and electrode; this is of particular benefit in samples from complex matrices which cause fouling of the electrode surface. The lifetime of the electrode is thus conveniently increased compared to a wall-jet detector in continuous flow.

### EXPERIMENTAL

A wall-jet cell adapted for BIA was used as described previously [1], and contained a glassy carbon disc electrode, diameter 0.5 cm<sup>2</sup>, a platinum gauze auxiliary electrode and an SCE reference. The micropipette tip (internal diameter 0.47 mm) was placed at a distance of 2mm over the centre of the disc electrode. A Rainin programmable electronic micropipette with three dispersion flow rates,  $V_f$ , maximum dispersion volume,  $V$ , of 100 $\mu$ l was employed, and a PAR273A potentiostat for controlling the experiments.

Mercury thin films were pre-formed *in situ* by the injection of 100 $\mu$ l of 10<sup>-1</sup>M mercury ion solution onto the electrode at -1.0V vs.SCE. Samples of the analyte solution were then injected and after preconcentration analysed by a square wave voltammetric scan in the determination step.

The ASV of zinc, cadmium, lead and copper was investigated as was the AdSV of nickel and cobalt using nioxime ligand.

### RESULTS AND DISCUSSION

The effects of injection rate, injection volume and preconcentration time were all investigated. As predicted from wall-jet theory, the slowest of the three possible injection rates was found to be most appropriate. A typical trace for cadmium and lead is shown in Fig. 1, illustrating the effect of preconcentration time,  $t_{dep}$ .

It was found that significant advantages arise from using a preconcentration time of the order of 30s, much longer than the injection time (~4s) which can be ascribed to diffusion of the electroactive species to the electrode remaining in the solution close to the electrode after injection, see Fig.2. At these preconcentration times, the dependence on increasing injection volume is not linear. This can be explained through the fact that the first part of the injected solution is pushed by convection sufficiently far from the

electrode so that it cannot reach the electrode by diffusion alone after the end of the injection period. Under these conditions, no significant increase in current in the determination step is obtained by injecting more than 50 $\mu$ l of sample solution.

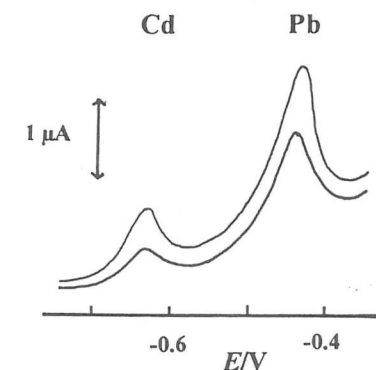


Fig.1 Typical traces for BIA-SWASV of cadmium and lead mixture.  $t_{dep}$ =50s at -1.0V;  $V=50\mu$ l;  $V_f=24,5\mu$ l s<sup>-1</sup>. Square wave parameters: amplitude 25mV, frequency 100Hz, scan increment 2mV. Cell contains 0.1M KNO<sub>3</sub>.  $[M^{2+}]$ = a:  $5 \times 10^{-8}$ M b:  $8 \times 10^{-8}$ M.

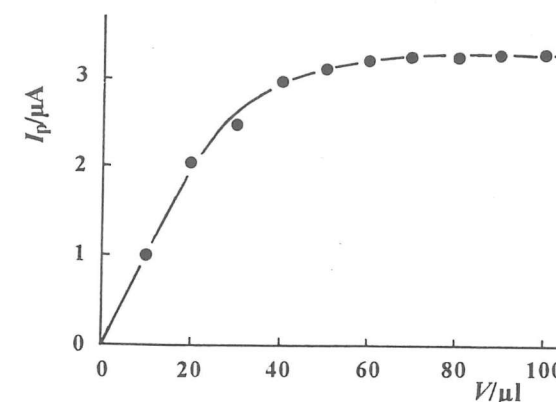


Fig.2 Effect of injection volume,  $V$ , on BIA-SWASV of lead; other experimental conditions as Fig.1.

Slopes of calibration curves for the batch injection anodic stripping voltammetry of zinc, cadmium, lead and copper are a factor of 100 less than that obtained at the wall-jet electrode in continuous flow [3]. This can be attributed to the effects of the lower volume of analyte solution, i.e. lower deposition time, and to the larger micropipette internal diameter (current proportional to its inverse square root). Nevertheless, a practical detection limit of 2nM is found and the linear range extends to 1 $\mu$ M

The adsorptive stripping voltammetry of nickel and cobalt ions using accumulation of the nioxime ligand on the mercury electrode has also been studied. A typical trace is shown in Fig.3.

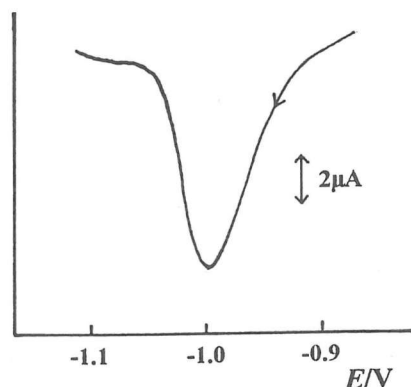


Fig.3 Typical trace for BIA-SWAdSV of cobalt-nioxime complex in 0.1M HEPES solution.  $t_{ads}=120s$  at  $-0.7V$ ,  $V_f=24,5\mu l s^{-1}$ ,  $V_s=100\mu l$ .  $[Co^{2+}]=10^{-7}M$ ;  $[nioxime]=10^{-4}M$ . Square wave parameters: amplitude 25mV, frequency 25Hz, scan increment 2mV.

Similar dependences on preconcentration time for adsorption,  $t_{ads}$ , and on injected volume were obtained as for ASV. Calibration curves were constructed and detection limits in the nanomolar region found, the linear range extending up to  $10^{-7}mol dm^{-3}$ .

Thus there are several advantages of BIA in conjunction with stripping voltammetry. Consumption of analyte sample is small ( $\leq 100\mu l$ ) and the contact time between sample and electrode is low - of particular benefit in samples from complex matrices which cause fouling of the electrode surface. Nanomolar detection limits are found. The technique is simple to use and is fast - under optimised conditions a minimum of 30 samples per hour can be analysed, usually without the necessity of addition of electrolyte to the sample before analysis.

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## VOLTAMMETRIC BEHAVIOUR OF SODIUM NITROPRUSSIDE IN AQUEOUS SOLUTION OF LOW pH EVIDENCES FOR COMPROPORTIONATION

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#### ABSTRACT

The electrochemical reduction of the pentacyanonitrosylferrate(II) ion ( $[Fe(CN)_5NO]^{2-}$ , nitroprusside ion) has been studied in aqueous solutions of low pH by polarography and cyclic voltammetry. There are consistent evidences for the existence of the protonated ion,  $[Fe(CN)_5NOH]^{2-}$ , electrochemically generated at the potential of the first reduction of the nitroprusside ion. Moreover, a fast regeneration of the reactant(s) of the second reduction process must be assumed, which, at high nitroprusside concentration, can be viewed as a comproportionation reaction between nitroprusside and the product of the second reduction in acidic media. The reduction products adsorb at the mercury electrode.

#### INTRODUCTION

The reduction of the nitroprusside ion, NP, has been intensively studied since the earlier 50's. However, the nature of the one-electron reduction products of NP has always been a matter of controversy<sup>1-4</sup>. It is now clear that the one-electron reduction, achieved either by chemical, electrochemical or radiolytic techniques, always produces, at least initially, the  $[Fe(CN)_5(NO)]^{3-}$  ion, where the nitrosyl ligand has been reduced. This species loses one  $CN^-$  ligand giving  $[Fe(CN)_4(NO)]^{2-}$ , which is the main product of the chemical or radiolytical reduction of NP<sup>4</sup>.

However, when NP is electrochemically reduced, Masek *et al.* proposed that the primary product,  $[Fe(CN)_5(NO)]^{3-}$  could also be protonated at the NO group<sup>1</sup>. They have studied the overall 4-electron electrochemical reduction of NP, a rather complex process, as shown in scheme 1. According to this scheme, in alkaline solution the main product of the one-electron reduction would be  $[Fe(CN)_4(NO)]^{2-}$  and in acidic solution the protonated ion,  $[Fe(CN)_5(NO)]^{2-}$ , would prevail<sup>1</sup>.