

Nafion-coated mercury thin film electrodes for batch-injection analysis with anodic stripping voltammetry

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Abstract

Batch-injection analysis exhibits the advantages of rapid and simple electroanalysis of microlitre samples. Nafion-coated mercury thin film electrodes have been evaluated for use in batch-injection analysis with anodic stripping voltammetry (BIA-ASV). The advantages of Nafion-coated electrodes in reducing electrode contamination by components of complex matrices are combined with the analysis of small microlitre sample volumes. The measurement of traces of lead and cadmium is used to illustrate the approach. An optimised procedure for formation of Nafion-coated mercury thin film electrodes is evolved. The relative sensitivity for BIA-ASV at electrodes with and without Nafion coatings is 0.9 and 0.8 for cadmium and lead respectively; detection limits are 2×10^{-9} M and 4×10^{-9} M. Studies were done concerning the influence of surfactants and their effect was found to be much less with the Nafion film coating. Applications to real environmental samples are demonstrated.

Keywords: Batch-injection analysis; Mercury film electrodes; Nafion-coated electrodes; Stripping voltammetry; Trace metals

1. Introduction

The batch-injection analysis (BIA) technique [1] was developed to enable the analysis of small ($\leq 100 \mu\text{l}$) volumes of liquid samples whilst retaining the advantage of convection in continuous

flow systems. Recent work involving electrochemical detection has demonstrated the similarities between amperometric detection in BIA and the response obtained at wall-jet electrodes in continuous flow [2]. This similarity arises because in both techniques a fine jet of solution (in the BIA case from a micropipette tip) impinges on the centre of a disc electrode immersed in electrolyte solution; this configuration means that memory

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effects are almost zero. The advantages of the use of a programmable, motorised electronic micropipette have been shown [2,3]. BIA with voltammetric detection has also been demonstrated [4]: consecutive injections during a slow potential sweep lead to a point-by-point voltammetric curve, and cyclic voltammetry and square wave voltammetry can be done during the injection itself.

BIA with stripping voltammetry is also an exciting possibility. After initial studies showing its viability [5], BIA with anodic stripping voltammetry (BIA-ASV) has been explored in detail and nanomolar detection limits were reached with good sensitivity using square wave stripping [6]. The mercury thin film electrode (MTFE) was formed *in situ* and the influences of injected volume, preconcentration time, and micropipette dispensation rate were investigated.

A particular benefit of the small sample volumes injected in BIA is that the contact time between sample and electrode is small. Problems of electrode fouling are thus reduced compared with continuous flow systems. Nevertheless, for complex matrices such as waste water with high surfactant levels and blood serum it is often necessary to reduce contamination even further, which can be done by suitable modification of the electrode surface.

Permselective electrode coatings have found use in reducing interference and contamination. Amongst those with applications in stripping voltammetry are Nafion (see e.g. Refs. [7–9]), cellulose acetate (see e.g. Ref. [10]) and dialysis membranes (see e.g. Ref. [11]). An additional benefit is the fact that any problems with adhesion of the mercury film to the glassy carbon substrate [12], which can occur under convective conditions, are removed.

Concerning Nafion films, the signal stability for differential pulse ASV was examined in detail for a number of Nafion-coated thin mercury film preparation methods [7], involving Nafion coating followed by mercury film deposition. Other work involved mixing a ligand specific for the metal ion to be determined, lead [8] and copper [9], with the solution of Nafion before coating.

The objective of this study was to reduce the interferences from complex matrices in the BIA-ASV technique through coating of the glassy carbon electrode with a thin Nafion film. Optimum experimental parameters are examined and comparison with results using a simple MTFE is presented. Application to trace metal determinations in environmental samples is described.

2. Experimental

A modified large open wall-jet cell constructed of perspex and filled with inert electrolyte was used as described previously [2]. The micropipette tip (internal tip diameter 0.47 mm) was fixed exactly over the centre of a glassy carbon (Tokai, GC-20) disc electrode, diameter 5 mm, at a distance of 2–3 mm. The cell also contained a platinum gauze counter electrode and a saturated calomel reference electrode.

A 5% solution of Nafion in low weight alcohols (Aldrich) was diluted with ethanol to prepare appropriate working solutions for forming the Nafion coatings. *N,N*-dimethylformamide (DMF) was of analytical grade (99.5%) and purchased from Fluka. The preparation of the Nafion-coated (NC) electrode is discussed below. Mercury films were made *in situ* by injection of 10 μl of a 10^{-1} M Hg(II) solution at -1.0 V applied potential. Unless stated otherwise the cell contained 0.1 M KNO_3 /0.002 M HNO_3 supporting electrolyte. Injections were performed using a programmable motorised electronic micropipette (EDP Plus 100 EP-100, Rainin Instrument Co. Inc.). This micropipette, of maximum dispensing volume 100 μl , has three dispensing rates; the BIA-ASV measurements were conducted at the slowest dispensing rate, which was calibrated in this study as 22.7 $\mu\text{l s}^{-1}$.

A computer-controlled EG&G PAR273A potentiostat with M270 Research Electrochemistry Software was used for running the electrochemical experiments.

Solutions were prepared from analytical-grade chemical reagents and Millipore Milli-Q ultrapure water (resistivity ≥ 18 M Ω cm). Stock solutions of 10^{-3} M Pb^{2+} and Cd^{2+} were prepared and di-

luted on the day as appropriate. The protein standard solution (Sigma) containing 0.5 g l^{-1} albumin and 0.3 g l^{-1} globulin; Triton X-100 (Sigma) and sodium dodecyl sulphate (SDS; Aldrich) were used as received in the corresponding studies after appropriate dilution. Experiments were conducted at room temperature ($25 \pm 1^\circ\text{C}$) and without deoxygenation.

2.1. Preparation of NCMTFE for BIA-ASV

Prior to polymer coating the glassy carbon electrode was polished using polishing foils with $0.3 \mu\text{m}$ alumina particles (Hirschmann, Germany), rinsed with Milli-Q water and allowed to dry.

The optimised procedure for forming the Nafion coating was as follows. First, $5 \mu\text{l}$ of 0.25% (w/v) Nafion solution was applied, followed immediately by $3 \mu\text{l}$ of DMF, to the electrode surface with a micropipette. The solvents were evaporated in a warm air stream from an air gun while the electrode was rotated at 50 rev min^{-1} . The polymer film was then cured for 60 s in a hot air stream (about 70°C), holding the gun just a few millimetres above the electrode surface. The studies which led to this procedure are described in the next section.

The NC electrode was then placed in the BIA cell and mercury deposition was done *in situ* by injecting $10 \mu\text{l}$ of a solution of 0.1 M Hg^{2+} in 0.1 M KNO_3 , 0.002 M HNO_3 and applying a deposition potential of -1.0 V during injection ($\approx 0.4 \text{ s}$) and a further 60 s after the end of the injection period. As previously shown [6], continuing to apply a potential corresponding to the electrode deposition reaction after the end of the injection itself significantly increases the electrolysis efficiency. The NCMTFE was then ready for use in ASV experiments.

3. Results and discussion

3.1. Optimisation of preparation methods of NCMTFEs

The procedure of Nafion coating and mercury deposition onto a glassy carbon electrode for use

in conjunction with BIA was studied with respect to practicality, the stability of the coating under the hydrodynamic conditions of BIA and the maximum attainable sensitivity for trace metal determinations.

There are two principal ways of preparing NCMTFEs. One possibility is to deposit mercury first followed by removal of the electrode from the plating solution and covering of the thin mercury film with a Nafion membrane under air [13]. Alternatively, the procedure can be reversed and the Nafion film prepared first followed by mercury deposition through the Nafion film [14]. The latter approach was found to be more convenient, particularly in a BIA arrangement; this is due to the fact that the mercury deposition can be performed *in situ* utilising the BIA approach [6]. In addition, covering a bare glassy carbon electrode with a Nafion film offers more freedom for varying the curing procedure parameters than in the presence of mercury, which may evaporate at higher temperatures.

Thus, the procedure of preparing the Nafion film first and then depositing mercury through the polymer film in the BIA cell was studied in detail with a view to optimisation of the relevant parameters. Initial studies used Nafion solutions alone for film formation, which led to films with a tendency to crack and have low adhesion. Previous studies suggested that the addition of a casting solvent can modify the properties of Nafion [15]. This was explored and it was found to be advantageous to employ DMF casting solvent and to heat during the formation of the Nafion film in order to improve its mechanical properties. In addition, preparing the Nafion film by spin-coating resulted in a more uniform polymer layer than under stationary conditions; a rotation speed of 50 rev min^{-1} was employed. For the size of the glassy carbon electrode used, 0.20 cm^2 area, $5 \mu\text{l}$ Nafion solution and $3 \mu\text{l}$ DMF were found to be appropriate.

The thickness of the Nafion film was varied using Nafion solutions of different concentration in the range 0.1–0.5% (w/v). The thinnest Nafion film made from 0.1% Nafion solution was found, after mercury deposition, to be insufficiently stable for BIA-ASV experiments. In contrast, using the

0.5% Nafion solution a stable Nafion film was obtained, but a substantial decrease in sensitivity for cadmium and lead determinations occurred in comparison with a MTFE without Nafion coating. As a compromise, employing a 0.25% Nafion solution yielded a film with sufficient stability under BIA conditions and acceptable relative sensitivities of 0.9 for cadmium and 0.8 for lead when compared with that for an uncovered MTFE (see below). Visually, the Nafion coating appeared transparent and uniform over the whole electrode surface, and resulted in homogeneous films without cracks, which was not possible without the addition of DMF casting solvent.

The above results led to the optimised procedure described in detail in Section 2.

3.2. Performance characteristics of BIA-ASV with NCTMFE

The determination of traces of cadmium and lead ions using square wave ASV was chosen in order to characterise the analytical features of the NCTMFE when incorporated in a BIA arrangement. Fig. 1 shows typical responses obtained for cadmium determinations in the concentration range 10^{-8} – 10^{-7} M. For both cadmium and lead the calibration plots were highly linear as expressed by the linear regression data given in Table 1 for the the ions analysed separately and as a mixture. Fig. 2 illustrates the good reproducibility of repetitive trace metal determinations. No memory effects were observed providing that between successive measurements an injection of electrolyte was done at a conditioning potential of

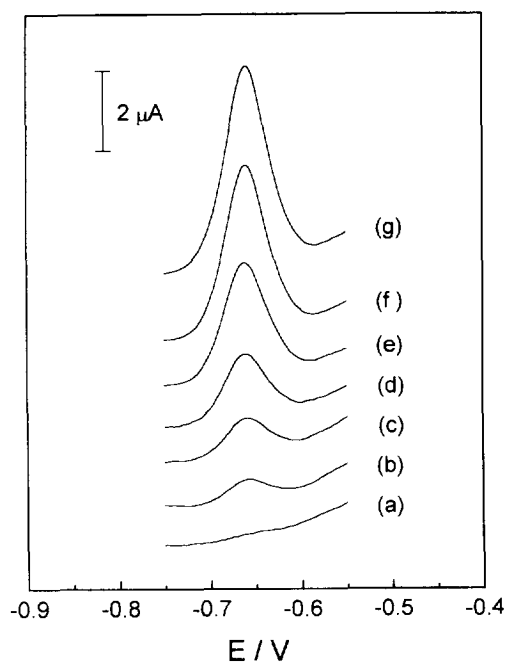


Fig. 1. Concentration dependence of the BIA-ASV response obtained for cadmium determinations with a NCTMFE. Experimental conditions: injection volume, 50 μ l; preconcentration, 30 s at -1.0 V vs. SCE; stripping mode, square wave voltammetry with amplitude 25 mV, scan increment 2 mV and frequency 100 Hz. Cadmium concentrations: (a) background; (b) 10^{-8} ; (c) 2×10^{-8} ; (d) 3×10^{-8} ; (e) 5×10^{-8} ; (f) 8×10^{-8} ; (g) 10^{-7} M.

-0.2 V to ensure the removal of electroactive species from the vicinity of the electrode surface. This potential was applied constantly between determinations. Detection limits were determined on the basis of the 3σ criterion related to the baseline noise level and amounted to 5×10^{-9} M

Table 1

Results of linear regression of calibration data for cadmium and lead determinations by BIA-ASV using a NCTMFE (Pb^{2+} : 1×10^{-8} – 1×10^{-7} M; Cd^{2+} : 5×10^{-9} – 1×10^{-7} M)

Analyte	Slope ($\mu\text{A nM}^{-1}$)	Intercept (μA)	Regression coefficient
Cd^{2+}	0.052	-0.07	0.9992 ($n = 7$)
Pb^{2+}	0.022	-0.01	0.9975 ($n = 6$)
Cd^{2+} (Pb^{2+}) ^a	0.042	0.09	0.9976 ($n = 5$)
Pb^{2+} (Cd^{2+}) ^b	0.023	0.05	0.9958 ($n = 5$)

^a Cadmium determinations in the presence of equal amounts of lead.

^b Lead determinations in the presence of equal amounts of cadmium.

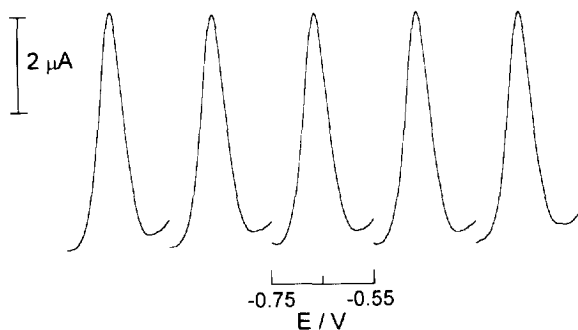


Fig. 2. Reproducibility of BIA-ASV determinations at a NCMTFE for a cadmium concentration of 10^{-7} M. Other conditions as in Fig. 1.

and 1×10^{-8} M for cadmium and lead respectively.

The stripping peaks corresponding to cadmium and lead using a NCMTFE appear at potentials 12 mV more negative than in the case of measurements at a MTFE without Nafion coating. This probably reflects the cation exchanging behaviour of the Nafion coating which favours the oxidised state of the test species. However, there was only a slight effect on the shape of the signals, the peak width at half height increasing from 52 to 55 mV, suggesting that any kinetic limitations due to the Nafion film are not important.

The above results are based on injections of 50 μ l of analyte solution and accumulation times of 30 s as suggested previously for BIA-ASV using an uncoated MTFE [6]. This was because, in the preconcentration step, the profile of signal height vs. injection volume reaches a maximum for this injection volume, due to the important contribution from diffusion to the electrode after the end of the injection itself of species remaining in the zone of the electrode. It was found during the course of this study that multiple injections of fractions of the total injection volume can lead to a further improvement in sensitivity using the multiple-dispense mode of the programmable micropipette without removing the pipette from the BIA cell. For example, four successive injections of 25 μ l analyte with short periods in between yielded about 2.5 times higher signals in comparison to a single injection of 50 μ l (note that an injection of 50 μ l gives the same signal as injec-

tion of 100 μ l, as explained above). The higher electrolysis efficiency obtainable via this multiple-injection approach is illustrated in Fig. 3 for BIA experiments using $K_4[Fe(CN)_6]$ oxidation as model reaction.

The multiple-injection technique was applied to trace metal determinations when the concentrations of the analyte species were close to the detection limit. In this way, the detection limit is reduced by a factor of 2.5 to 2×10^{-9} M and 4×10^{-9} M for cadmium and lead respectively. The analytical utility of this approach is demonstrated in Section 3.4.

3.3. Influence of matrix constituents on the BIA-ASV response

The effects of various organic surfactants on the response of the NCMTFE in BIA-ASV measurements were studied using cadmium as test analyte. Some common surface-active compounds, such as Triton X-100, and a protein

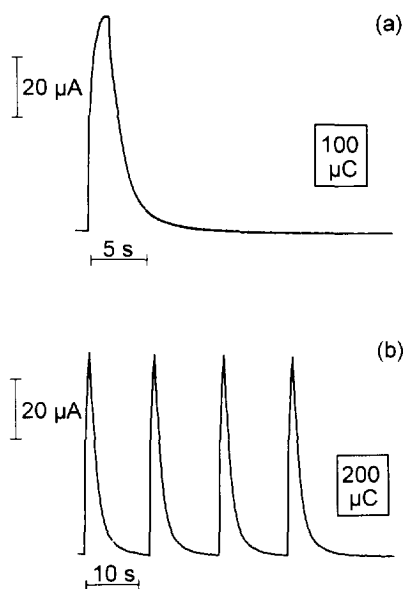


Fig. 3. BIA response for amperometric detection at +0.6 V vs. SCE for oxidation of 2 mM $K_4[Fe(CN)_6]$ in 0.4 M K_2SO_4 electrolyte using a bare glassy carbon electrode. The amperometric transient (a) corresponds to an injection of 50 μ l of $K_4[Fe(CN)_6]$ solution while (b) represents the response for four consecutive injections of 25 μ l analyte solution. The dispensing rate is 22.7μ l s^{-1} in both cases.

Table 2

Effects of surface-active compounds on the BIA-ASV response for 50 μl injections of 10^{-7} M Cd^{2+} at a MTFE and a NCMTFE

Surface-Response active compound		c (mg l^{-1})				
		1	2	5	11	22
Triton X-100	ΔI_p (%) MTFE	-12	-21	-37	-81	-91
	ΔI_p (%) NCMTFE	-14	-17	-24	-37	-76
SDS ^a	ΔI_p (%) MTFE	-14	-19	-24	-26	-27
	ΔI_p (%) NCMTFE	-3	-9	-	-20	-23
Protein standard	ΔI_p (%) MTFE	-	-8	-15	-20	-68
	ΔI_p (%) NCMTFE	-	-5	-6	-6	-6

^a The measurements were performed in 0.1 M acetate buffer (pH 4.5).

standard, were chosen as representing different types of interference with faradaic electrode processes. The effects of the individual surfactants on the BIA-ASV response were examined with both the MTFE and the NCMTFE in order to obtain a direct comparison under identical conditions. The experimental approach used was to inject first a sample containing 10^{-7} M cadmium ions (without the surfactant) onto a newly prepared electrode. Next, samples containing the same concentration of metal ions but in the presence of increasing concentrations of surfactant were injected consecutively. Table 2 summarises the relevant results of these measurements. In all cases, the NCMTFE was clearly less susceptible to peak depression than the MTFE. As an example, Fig. 4 illustrates the different extent of signal depression due to the presence of Triton X-100 for (A) a MTFE and (B) a NCMTFE. In particular, the results obtained for samples with a matrix containing proteins indicate that the Nafion coating is an effective barrier to the transport of these potential interferents towards the mercury surface, which agrees with data found previously by other authors [14,16–18]. The slight decrease in the BIA-ASV signal of 5 or 6% obtained with the NCMTFE after additions of protein standard to the sample was even independent of the protein concentration in the range studied up to 22 mg l^{-1} . Thus, it can be speculated that the measured decrease in signal results from complexation of the analyte [19] rather than from electrode blocking effects.

3.4. Practical applications

The analytical utility of the NCMTFE in conjunction with BIA-ASV was investigated by applying it to the analysis of heavy metal traces, lead and cadmium, in environmental samples with complex matrices, using the standard addition method.

Fig. 5 illustrates the results obtained for an undiluted waste water sample using the technique of multiple standard additions and the evaluation of cadmium concentration—these samples were found not to contain lead at a detectable concentration. The rather low concentration of 5.0 ± 0.1

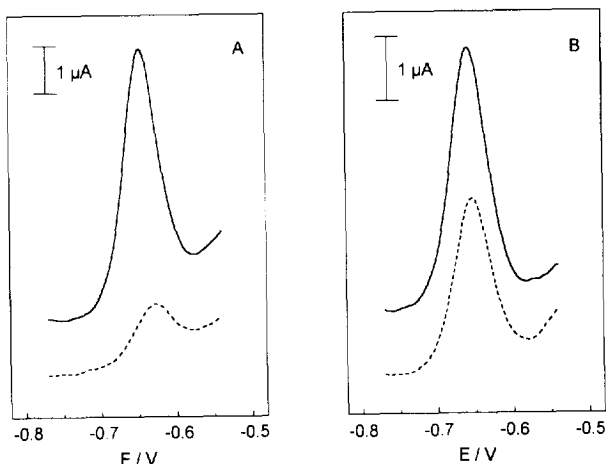


Fig. 4. BIA-ASV signals obtained with (A) MTFE and (B) NCMTFE for injections of samples containing 10^{-7} M Cd^{2+} in the absence (solid line) or in the presence (broken line) of 11 mg l^{-1} Triton X-100 surfactant. Other conditions as in Fig. 1.

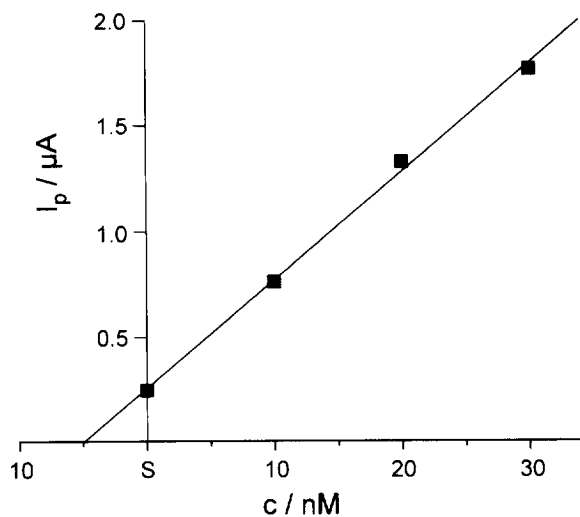


Fig. 5. Evaluation of the cadmium determination in an undiluted waste water sample by BIA-ASV with a NCMTFE using the standard addition method. The signals for the original sample (S) and that obtained after standard addition correspond to a multiple-injection preconcentration of four consecutive injections of 25 μ l within a total preconcentration period of 60 s.

nM (0.56 ± 0.1 ppb) cadmium showed the advantages of using the multiple-injection preconcentration procedure described above in order to increase electrolysis efficiency. Repetitive measurements showed almost no changes in the voltammetric response, which indicates effective protection of the NCMTFE against interfering matrix constituents.

In addition, a sample was taken from a car wash, which obviously contained a high amount of detergents. In this case, lead traces were quantified in this sample using multiple-injection preconcentration but no detectable traces of cadmium were encountered. The NCMTFE was not completely insensitive to the matrix constituents as indicated by a progressive signal decrease of the BIA-ASV response of a few percent for repetitive measurements. However, the technique of standard addition requires just a limited number of measurements and the contact time of the sample matrix with the electrode surface in the BIA mode is very short. Consequently, a lead concentration of 15.5 ± 0.9

nM (3.2 ± 0.2 ppb) was determined on the basis of measuring the signal from the sample solution and performing two standard additions for which the electrode characteristics can be assumed to remain constant.

Confirmation of the values was obtained by AAS with electrothermal atomization. The waste water sample led to 0.6 ppb and <0.05 ppb and the car wash sample to 0.15 ppb and 3.0 ppb for cadmium and lead respectively. The levels of lead in the first case and cadmium in the second are below BIA-ASV detection limits. Since electrochemical methods probe the amount of labile species in a given oxidation state rather than the total amount of the element as in AAS, the agreement between BIA-ASV with standard addition and AAS shows that in the samples tested all the metal ions are present in a labile form. In other cases, where a fraction of the metal ions is not labile, the electrochemical response will be lower, and standard addition will measure the concentration of these labile species.

For the environmental samples studied the performance characteristics of the NCMTFE were far superior to those of the MTFE with regards to fouling of the electrode surface by contaminants in complex matrices and the improved stabilisation of the mercury film. In fact, it was impossible to obtain meaningful results concerning the lead concentration in the car wash sample when using a bare MTFE.

4. Conclusions

It has been shown that NCMTFEs offer significant advantages compared to ordinary MTFEs for square wave ASV using the BIA technique, and these are particularly evident in the analysis of environmental sample containing high surfactant levels. The technique for the formation of the NCMTFE is simple. This, combined with the easy and rapid BIA-ASV procedure, demonstrates that it will be an important method for the determination of small (microlitre) volumes of traces of heavy metals in complex matrices.

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