Novel polymer-modified electrodes for batch injection sensors and application to environmental analysis☆

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Abstract

Various polymer coatings have been investigated for the protection of mercury thin-film electrodes in the square wave anodic stripping voltammetry of environmental samples using batch injection analysis, with injection of untreated samples of volume 50 μl directly over the sensing electrode. Polymer coatings studied include those with controlled porosity, and cation-exchange polymers based on sulphonated polymers. Of the polymers tested, films of ca. 1 μm thickness made from Nafion® mixed with 5% poly(vinyl sulphonic acid) were found to give the best results in tests with the model surfactants Triton-X-100 detergent, sodium dodecyl sulphate and protein standard. The validity of the approach is demonstrated by application to real samples. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Two of the challenges regarding the application of electrochemistry to environmental analysis are to be able to undertake analyses without any sample pretreatment or addition of electrolyte and, as far as possible, to obtain a response in real time.

General sample pretreatment procedures include acid mineralization, ultraviolet radiation and microwave digestion [1]. Apart from the time taken for results to be obtained, the speciation of the system is destroyed. Sensitive techniques such as atomic absorption spectrometry, neutron activation analysis and plasma emission spectrometry give no information on chemical speciation; they can only do so if used in conjunction with other analytical operations such as solvent extraction, chromatography, electrophoresis, dialysis etc. [2–4]. After sample pretreatment and digestion, measurements of the quantity of elements obtained through techniques such as atomic absorption spectrometry should be the same as those from electrochemical techniques.

Electroanalysis offers the possibility of measuring the concentration of labile species in a given oxidation state without pretreatment and digestion, particularly appropriate in the case of metal cations [5–7]. For this approach to be viable, it is necessary that the electrode surface not be blocked by the adsorbable interferents, which would be removed in mineralization or digestion procedures. Two ways can be envisaged towards solving this problem: protection of the electrode surface against irreversible adsorption, whilst permitting the electrode reactions of interest to occur, and minimization of the time of contact between sample and electrode through the use of injection techniques.
In a real situation, continuous on-line monitoring may be necessary, using detectors such as a wall-jet electrode [8], in which case electrode protection is extremely important. Contact time between sample and electrode can be reduced by the technique of batch injection analysis (BIA) [9–11], which involves the injection of samples of volume 100 μl over the centre of an electrode immersed in electrolyte solution. This approach has the added advantage of there being no carrier stream as in flow injection analysis [12] and sample dispersion is close to zero. An additional advantage of the wall-jet hydrodynamics in BIA [11] is that there is no memory effect, since only freshly arriving solution can reach the electrode surface.

The technique of BIA has been applied to the analysis of nanomolar traces of heavy metal cations at mercury thin film electrodes on glassy carbon substrates using square wave anodic stripping voltammetry (SWASV) [13,14]. In the analysis of environmental samples, even of natural waters, it was already noted a number of years ago that irreversible adsorption of surface-active components on the electrode causes a progressive decrease of response, e.g. [15,16]. Although blocking and fouling of the electrode surface is less with BIA than with continuous flow, owing to the small contact between sample and electrode, over a period of time contamination effects on the mercury surface do occur. For this reason, protective coatings which avoid electrode blocking need to be developed.

Polymer coatings for discriminating against electrode fouling in ASV can exhibit ion-exchange characteristics, such as Nafion®-based coatings e.g. [17,18] or controlled porosity coatings, such as cellulose acetate, e.g. [19,20]. Initial studies by us with cellulose acetate films, hydrolysed to various degrees, in BIA-SWASV experiments were relatively unsuccessful. However, thin films of the cation exchange polymer Nafion® gave promising results [21]. The influence of a number of different types of surface-active contaminants was investigated in the determination of metal cations by BIA-SWASV, namely detergents, polyelectrolytes and proteins. The Nafion® film also served to hold the mercury ‘film’ in place, which in fact consists of a large number of closely-spaced mercury droplets. This aspect is particularly important if an ultrasound probe is employed to transport species to the electrode, the ultrasound further reducing any blocking due to its cleaning effect [22].

In this paper polymer film coatings for the measurement of metal cations in untreated samples using BIA have been optimised through the use of polymers of different porosity characteristics or of mixtures of Nafion® with other polymers, and a careful study of experimental conditions has been carried out.

2. Experimental

Experiments were all conducted using a large open wall-jet cell modified for batch injection analysis, as described previously [11]. The disc working electrode (diameter 0.5 cm) was of glassy carbon (Tokai, GC20), the auxiliary electrode was platinum gauze and a saturated calomel electrode served as the reference (Radiometer K401). The cell, of volume 40 cm³, was filled with inert electrolyte, as specified below. Samples were injected from a Rainin EDP-Plus 100 motorised programmable electronic micropipette, with calibrated flow rates of 24.5, 47.6 and 75.3 μl s⁻¹, which permits injections of volumes between 10 and 100 μl; the tip diameter was 0.47 mm and was placed 2–3 mm above the centre of the working electrode. Solutions were made from analytical grade reagents and Millipore Milli-Q water (resistivity ≥ 18 MΩ cm).

Experiments were conducted using a BAS CV-50W potentiostat (Bioanalytical Systems, W. Lafayette, Indiana, USA) controlled by Model 2.0 software.

Polymer coatings included cellulose acetate hydrogen phthalate (CAHP) (Aldrich) and poly(methyl methacrylate-co-hydroxyethyl methacrylate) (PMMA-HEMA) with monomer ratio 2:1 or 10:1 (monomers from Aldrich). In the case of CAHP, 5 μl of a 0.25 wt.% solution in cyclohexanone + acetone 1:1 was applied to the electrode surface, the solvent was allowed to evaporate, and was then hydrolysed for 16 min. in 0.08 M NaOH.

PMMA-HEMA was prepared by chemical co-polymerization according to standard procedures. Volumes of 5 cm³ each of the pure monomers MMA and HEMA were mixed with 90 cm³ water, and 100 mg potassium persulphate initiator. The polymerization reaction was carried out at 50°C for 12 h. After filtering and drying, the co-polymer was dissolved in acetone and the solvent allowed to evaporate so as to form solid membranes. The membranes, thickness ca. 100 μm, were then hydrolysed in 1.0 M NaOH for 2 h and following this dissolved as a 0.25 wt.% solution in acetone, 1:1 ethanol + acetone or 1:1 cyclohexanone + acetone. A volume of 5 μl of the 0.25 wt.% solution was applied to the electrode surface and then left to dry for 25 min.

Polymerisation of sulphonate-containing monomers was also carried out chemically. A volume of 4 cm³ of vinyl sulphonric acid or styrene sulphonlic acid was dissolved in 10 cm³ of a 1:1 mixture of ethanol and water. To this solution was added 100 mg of potassium persulphate initiator and the reaction was carried out at 50°C for 24 h. The polymers were precipitated in methanol:diethyl ether (5:1) and the solid was filtered under vacuum and dried. The procedure for making copolymers of vinyl sulphonlic acid with either styrene or maleic anhydride was the same except that 2 cm³ of each monomer was used. In all cases the molar mass of
the polymers prepared in this way was determined to be greater than 40 000 g mol\(^{-1}\).

For making Nafion\textsuperscript{®}-based films, a 5 wt.% Nafion\textsuperscript{®} solution in low-weight alcohols and water (Aldrich) was diluted to 0.25 wt.% in ethanol and mixed in the desired proportion with a 0.25 wt.% solution of the other polymer in water. A volume of 5 μl was then applied directly onto the glassy carbon electrode, followed immediately by 3 μl of \(N,N\)-dimethylformamide casting solvent. The solvents were evaporated in a warm air stream from an air gun while the electrode was rotated at 50 rpm for 30 s; the polymer was then cured for 60 s in a hot air stream (ca. 70°C).

The coated electrode was placed in the BIA cell and mercury deposition was done in situ by injecting 10 μl of a solution of 0.10 M Hg\textsuperscript{2+} in 0.10 M KNO\(_3\) + 5 mM HNO\(_3\). The applied potential was −1.0 V versus SCE for 64 s. MTFEs prepared in this way could be used for a series of SWASV experiments over one day without electrode renewal. SWASV experiments were done by preconcentrating the metal ions at the applied potentials and for the accumulation times to be specified below followed by a square wave positive-direction stripping scan with square wave parameters of amplitude 25 mV, potential step increment 2 mV and frequency 100 Hz, corresponding to an effective scan rate of 200 mV s\(^{-1}\).

3. Results and discussion

Two types of polymer coating were tested based on size exclusion and based on cation exchange. As will be demonstrated, both of these lead to satisfactory results in ideal conditions. However, differences in mechanical stability lead to difficulties in the application of size-exclusion polymers.

Some general comments should first be made regarding the BIA-SWASV procedure. The stripping peak current is proportional to the concentration of electroactive species and thence to the charge accumulated during the pre-concentration step. At a bare electrode the amount of charge accumulated for pre-concentration during injection, assuming that the applied potential is that for diffusion-limited reduction, is given by wall-jet hydrodynamics and leads to an electrolysis efficiency of [14]:

\[
\eta(I) = 1.39 \nu^{-5/12} D^{2/3} V_r^{-1/4} R^{3/4} a^{-1/2}
\]  

(1)

where \(\nu\) is the kinematic viscosity (ca. 10\(^{-2}\) cm\(^2\) s\(^{-1}\)), \(D\) the diffusion coefficient (ca. 10\(^{-5}\) cm\(^2\) s\(^{-1}\)), \(V_r\) the flow rate (ca. 40 μl s\(^{-1}\)), \(R\) the electrode radius (ca. 0.25 cm) and \(a\) the jet diameter (ca. 0.05 cm). For the typical values of the experimental parameters shown in brackets in this type of ASV experiment in aqueous solution, \(\eta(I)\) is ca. 0.7%. If deposition is continued after the end of the injection, so that species remaining in the zone of the electrode can be accumulated, then the efficiency can be increased by a factor of ca. two to 1.5%. This also shows the benefit of employing the slowest injection rate of 24.5 μl s\(^{-1}\), as used in all experiments to be described below. Regarding the volume of the injected sample, it was found that 90% of the maximum stripping current response is reached for an injection volume of 50 μl [14,21]; the explanation for this is the large contribution to the total amount accumulated from the species remaining in the electrode zone—for larger injection volumes, the unreacted species from the initial part of the injection have been convectively transported too far away from the electrode surface to diffuse back.

The presence of polymer coatings will reduce the value of \(\eta(I)\) and may serve to retain some of the sample within the polymer coating during the stripping
Table 1
Data regarding polymer film formation on glassy carbon electrodes using a mixture of 20% polymer and 80% Nafion®; both of concentration 0.25% mva

<table>
<thead>
<tr>
<th>Polymer added to Nafion®</th>
<th>Visual aspect of Nafion®/polymer solution</th>
<th>Preparation of film</th>
<th>Integrity of film after 15 injections b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVSA</td>
<td>Limpid</td>
<td>Easy</td>
<td>Good</td>
</tr>
<tr>
<td>PVSA-MA</td>
<td>Cloudy</td>
<td>Easy</td>
<td>Good</td>
</tr>
<tr>
<td>PVSA-S</td>
<td>Cloudy</td>
<td>Difficult</td>
<td>Peeling off</td>
</tr>
<tr>
<td>PSSA</td>
<td>Limpid</td>
<td>Easy</td>
<td>Good</td>
</tr>
</tbody>
</table>

a PVSA, poly(vinyl sulphonic acid); PVSA-MA, poly(vinyl sulphonic acid–co-maleic anhydride); PVSA-S, poly(vinyl sulphonic acid–co-styrene); PSSA, poly(styrene sulphonic acid).
b To assess the film integrity, the electrode was removed from the cell and inspected visually and by optical microscope.

scan. There may be a need for an injection of electrolyte between sample injections to clean the zone of the electrode; it was found to be beneficial to perform this routinely.

3.1. Size exclusion polymers

Size-exclusion polymers investigated include cellulose acetate hydrogen phthalate (CAHP) and poly(methyl methacrylate-co-hydroxyethyl methacrylate) (PMMA-HEMA), monomer ratio 2:1 or 10:1. Preparation of the films was as described in the experimental section.

Experiments with 0.1 M Pb⁺⁺ in acetate buffer were carried out in order to evaluate the effectiveness of the various polymer coatings. For PMMA-HEMA (2:1) coated MTFEs, the response obtained for injection of lead ions was significantly influenced by diffusion limitations through the polymer coating, the signals being less than 20% of those obtained at the uncovered MTFE. This was despite the coating thickness being only of the order of 2 μm, as estimated from optical microscopy observations, by putting the substrate or polymer film surface in focus.

In the case of both CAHP and PMMA-HEMA (10:1) films, the signal was reduced to ca. 25% compared to that obtained at the uncovered MTFE. For PMMA-HEMA (10:1) the results were dependent on the solvent, due to the different morphologies and structures of the polymer coatings. In the case of acetone solvent, solvent evaporation was rapid which led to non-uniform films, parts of which were opaque. A progressive decrease in solvent volatility was achieved by mixing acetone with ethanol or cyclohexanone in a 1:1 ratio leading to visually uniform films in both cases, with slight opaqueness, with spreading over the electrode surface being better in the latter case. Additionally, making the mercury film following the procedure described in the experimental section led to more homogeneous films for the cyclohexanone + acetone solvent. Thus, in further work, a solution of 0.25 wt.% CAHP or 0.25 wt.% PMMA-HEMA 10:1 in cyclohexanone + acetone was employed.

A typical response for the analysis by BIA-SWASV of zinc, cadmium, lead and copper at PMMA-HEMA films under these conditions is shown in Fig. 1. It can be seen that whereas the response for cadmium and lead are well-defined symmetrical peaks, those of zinc and copper are more difficult to quantify owing to the sloping baseline. For cadmium (E_p = 0.65 V) and lead (E_p = 0.48 V), although detection limits (defined as 3σ) of 7.0 and 0.52 nM, respectively, are reasonable, calibration plots give non-zero intercepts and there is some lack of reproducibility between films. The main reason for this lack of reproducibility can be attributed to the lack of physical and mechanical stability of the polymer films. First it was not easy to prepare uniformly thick films, and secondly, the coatings showed a tendency to crack due to poor adhesion after repeated injections. The fact that the detection limit is much higher for cadmium also reflects the fact that the stripping currents were a factor of two lower than for lead. Such a difference in response has been noted before. For these reasons, it was decided to return to Nafion®-based coatings [21] and improve their properties by using mixtures of polymers or using those of similar structure.

3.2. Cation exchange coatings

The electrode preparation procedure described in [21] and in the experimental section was further optimised for the measurement of cadmium and lead ions, and tested with model interferents—Triton-X-100, sodium dodecyl sulphate (SDS) and protein standard (5.0 g dl⁻¹ albumin and 3.0 g dl⁻¹ globulin, Sigma). In order to eliminate the possibility of any influence from electrode blocking by the surfactants, an injection of electrolyte, equal to that in the cell, was always done between successive sample injections; this was tested and found to be effective. A typical trace obtained at a Nafion®-coated mercury thin film electrode (NCMTFE) is shown in Fig. 2. In [21] the most significant reductions in current of 76% were obtained with 22 mg l⁻¹
Triton-X-100 for cadmium; this was now decreased to 27% with 20 mg l$^{-1}$ Triton-X-100: such results are similar to those in [23]. The origin of this improvement can be ascribed to better film formation, principally a slower curing procedure using a temperature of around 50°C.

In order to attempt to improve the cation-exchange ability of the coatings, other sulphonate-containing cation exchange polymers were considered with a higher concentration of sulphonate groups, identified in Table 1. The difficulty arising from the use of such polymers is their high solubility in water. Solubilities in water of the prepared polymers were measured, and it was concluded that none of them could be applied as a robust electrode coating. It was therefore decided to mix their aqueous solutions with a Nafion$^\text{®}$ solution in low-weight alcohols and apply this mixture to the electrode surface, usually 20 with 80% Nafion$^\text{®}$ solution, each component having a concentration of 0.25 wt.%, following the procedure described in the experimental section. Some of the characteristics regarding the films are shown in Table 1.

A possible difficulty with the use of such mixed-polymer coated electrodes is the loss of the polymer from the Nafion$^\text{®}$ matrix. This was tested by weighing free-standing membranes accurately, leaving them in electrolyte for a whole day; after rinsing and drying they were weighed again, there being no weight loss. Additionally, there was no change in voltammetric response of coated electrodes over the same time period.

In Fig. 3 are shown typical results (mean of three readings with blank electrolyte injection between each, relative standard deviation 3%) obtained for the addition of Triton-X-100 detergent to samples containing Cd$^{2+}$ (Fig. 3(a)) and Pb$^{2+}$ (Fig. 3(b)) as analysed by BIA-SWASV for various types of coating containing sulphonate polymer mixed with Nafion$^\text{®}$. The dotted line shows the responses obtained at the bare MTFE. Apart from Nafion$^\text{®}$ itself, all polymer coatings contained 20% of the sulphonate polymer except for one case in which 5% PVSA was used—the reason was that the stripping current for analysis of cadmium ions decreased dramatically for this polymer mixture without surfactant and to a much greater extent when more than 2 ppm Triton-X-100 were added. A percentage of 5% PVSA led to improved results, in terms of larger stripping signals under the same SWASV experimental conditions, as seen in Fig. 3. Several points become clear on examination of these plots.

- Although the percentage alteration in some of the signals on addition of different types of surfactant is small, the signal without surfactant is also different. This reflects the structure of the polymer film on the electrode surface, and its influence on diffusion. It is particularly evident for Nafion$^\text{®}$/PVSA-MA for both cadmium and lead ions.
Regarding Triton-X-100 detergent, percentage alterations are small in some cases, but the current in the absence of detergent varies considerably. The percentage variations are shown in Tables 2 and 3 for cadmium and lead, respectively.

A specific interaction is seen between Triton-X-100 and Pb\(^{2+}\), such that the stripping current increases as small concentrations of Triton-X-100 are added and then levels off. This has been noted previously [23].

Another important point is the possible influence of the electrolyte, an example being the membrane made from Nafion®/PVSA (80:20) mixture as shown in Fig. 3(a), and referred to in Table 2. The reduction of signal reduction can thus be ascribed to complexation and interferents in solution.

These studies showed that electrodes coated with a film containing 95% Nafion® and 5% PVSA showed the best performance in minimizing the influence of Triton-X-100 on the response.

Thus, experiments with SDS and protein standard were carried out using Nafion®/PVSA (95:5) films. Fig. 4 shows results obtained for Cd\(^{2+}\) and Pb\(^{2+}\), with the current scale expanded to show any differences more clearly. As expected from previous work [21], the influence of surfactant in these cases is much less than with detergents. Calibration plots gave detection limits in the same range as for samples with detergent. Nevertheless, protein-Pb\(^{2+}\) interactions are more significant than protein-Cd\(^{2+}\) interactions or interactions between the cations and the other surfactants, and the current drops by ca. 20% for 20 mg l\(^{-1}\) protein. This is a slightly larger effect than for Nafion® by itself, and which may be due to electrostatic interactions and ion association. These observations are in themselves interesting and suggest further studies in probing protein-Pb\(^{2+}\) interactions and also Triton-X-100-Pb\(^{2+}\) interactions as described above.

### 3.3. Application to real samples

Application of these polymer-coated electrodes was demonstrated by the analysis of real environmental samples using Nafion®-coated electrodes. Samples were taken from an open-air effluent rivulet at the edge of an environment.

<table>
<thead>
<tr>
<th>Triton-X-100/[mg l(^{-1})]</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>34</td>
<td>14</td>
<td>10</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Nafion®/PVSA (80:20)</td>
<td>45</td>
<td>39</td>
<td>82</td>
<td>69</td>
<td>70</td>
</tr>
<tr>
<td>Nafion®/PVSA (95:5)</td>
<td>-4</td>
<td>-2</td>
<td>6</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Nafion®/PVSA-MA (80:20)</td>
<td>52</td>
<td>80</td>
<td>54</td>
<td>29</td>
<td>14</td>
</tr>
</tbody>
</table>

*a* \([I_{p0} - I_{p0,0}] / I_{p0,0} \times 100\); \(I_{p0}\) and \(I_{p0,0}\) are stripping peak currents before and after addition of Triton-X-100; deposition time 30 s at \(-1.0\) V vs. SCE. 

\[\text{0.1 M Acetate buffer, pH 4.6.}\]
industrial zone (sample S1) and from a river (sample S2). The determined levels of zinc, cadmium, lead and copper are shown in Fig. 5 using the standard addition analysis method, using 50 μl injections of the samples. These correspond to analysis of raw samples after collection but without sample pre-treatment (white bars), and after acid digestion for 48 h by addition of HNO₃ at pH 1.8 (grey bars). Note the difference in concentration scale between samples S1 and S2 of a factor of twenty higher in the former case. The quantities of labile cadmium in sample 1 and of copper in sample 2 were below the detection limits and so are not represented.

Although the organic content of these effluents is visually obvious and sample solution S1 was not limpid, it was found that for these samples there was no difference between results obtained at Nafion®-coated and Nafion®/PVSA-coated electrodes. The generally higher levels after acid digestion are those obtained by

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**Fig. 4.** Plots showing the influence of increasing (a) SDS and (b) protein concentration on the BIA-SWASV stripping peak current at Nafion®:PVSA (95:5)-coated MTFEs for 10⁻⁷M (●) Cd²⁺ and (■) Pb²⁺. Experimental parameters as in Fig. 1.

**Fig. 5.** Standard addition analysis of environmental samples using BIA-SWASV at NCMTFE: S1 effluent from industrial zone, S2 from small river. Results are shown immediately after collection (pH indicated) and after 48 h digestion at pH 1.8 (addition of nitric acid).
other analytical techniques, as checked by atomic absorption spectrometry (differences < 3%) and reflects an increase in the concentration of labile cations. It can be seen that a rapid and useful diagnostic can be obtained through the electrochemical method.

4. Conclusions

The technique of batch injection analysis offers a relatively simple and powerful method for the analysis of trace metals in environmental samples. Effective protection of the electrode surface by thin Nafion®-based polymer coatings does not significantly reduce the electrode response and permits the repeated determination by square wave stripping voltammetry of the labile fraction of common heavy metal ions in the presence of surfactant interferents. These results augur well for application of the technique in the field as an important diagnostic tool as well as to detailed studies in the laboratory.

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