Article

Modified Electrode Voltammetric Sensors for Trace Metals in Environmental Samples

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Eletrodos de filmes finos de mercúrio modificados com Náfion foram investigados para análise de traços de metais em amostras ambientais de águas e efluentes, pela combinação das técnicas de análise por injeção de fluxo descontínuo e de voltamentria de onda quadrada com redissolução anódica. O método, envolvendo injeção de cerca de 50 microlitros de amostras sem tratamento prévio sobre o eletrodo detector, apresenta resposta rápida. O bloqueio e o envenenamento do eletrodo são mínimos, como mostram os estudos com componentes tensoativos. Foi realizada uma comparação entre substratos de carbono vítreo e de rede de microeletrodos de fibra de carbono, com este último apresentando um pequeno aumento de sensibilidade. Como aplicação foram analisadas amostras de água de rio e de efluentes industriais, coletadas e digeridas em meio ácido para a determinação de íons zinco, cádmio, chumbo e cobre.

Nafion –modified mercury thin film electrodes have been investigated for the analysis of trace metals in environmental samples of waters and effluent by batch injection analysis with square wave anodic stripping voltammetry. The method, involving injection over the detector electrode of untreated samples of volume of the order of 50 microlitres has fast response, blocking and fouling of the electrode is minimum as shown by studies with surface-active components. Comparison is made between glassy carbon substrate electrodes and carbon fibre microelectrode array substrates, the latter leading to a small sensitivity enhancement. Application to analysis of river water and industrial effluent for labile zinc, cadmium, lead and copper ions is demonstrated in collected samples and after acid digestion.

Keywords: polymer-modified electrodes, trace metal analysis, batch injection analysis, environmental monitoring

Introduction

The use of voltammetric sensors in environmental analysis requires the protection of the electrode surface from blocking effects of adsorbable components in the sample matrix[1]. If this is not done, then the signal can rapidly decrease to zero and the electrode surface has to be renewed; this is a significant drawback at solid electrodes. We have recently addressed this important problem, particularly for electroanalysis of effluents, in two ways. First, the volume of analyte has been reduced to ≤100 microlitres using the batch injection analysis (BIA)[2] technique: samples are injected directly over the centre of a detector electrode immersed in electrolyte solution. The small volume of analyte sample helps to reduce contamination effects. An additional advantage of this approach is that dilution of the sample with electrolyte is unnecessary. Secondly, the electrode surface is protected by a polymer coating to minimise blocking by irreversible adsorption. Particular emphasis has been given to the determination of trace metals at mercury thin film electrodes in complex matrices as found in environmental samples, when cation exchange polymer coatings can be employed[3,4]. The combination of BIA with square wave anodic stripping voltammetry (SWASV) has been shown to be particularly advantageous for trace metal ions[5]. Polymer coatings have included Nafion[6], poly(ester sulphonic acid)[7] and various mixtures of highly sulphonated polymers with Nafion[8]. Although specific benefits arise from the latter two types of coating, in terms of discrimination against potential interferents –

mainly surfactants – for most cases Nafion is found to be sufficiently good. This is because the importance of such analyses will be as a diagnostic tool for the presence of metal ions in the field; more accurate analyses can then be undertaken in the laboratory under improved conditions.

Thus in this paper, the use of the BIA-SWASV technique is evaluated for application to the analysis of real environmental samples. Comparison is also made between mercury thin-film electrodes on glassy carbon substrates and a mercury microelectrode array formed on a "random array of microdisks (RAM)" of carbon fibres. Recent work[9] has shown that such electrodes offer interesting properties which can be exploited in specific situations.

Experimental

The BIA cell was as described earlier[10] and is made of Perspex, filled with approximately 40 cm[3] of electrolyte. The working electrode is inserted through an opening in the middle of the bottom of the cell and sealed with an O-ring. In this work the electrode was a glassy carbon disc, diameter 5 mm, in a Teflon sheath or a carbon fibre RAM electrode (600 active microdisks of 3.5 μm diameter embedded in epoxy resin - CSIRO, Melbourne, Australia). The cell also contains a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference. Injections were done from a programmable, motorised, electronic micropipette (EDP Plus ED-100, Rainin Instrument Co. Inc.). The micropipette tip, internal diameter 0.47 mm, is fixed vertically through the cell lid directly above the centre of the working electrode at a distance of 2-3 mm. During injections, wall-jet hydrodynamics apply, as has been verified[10].

Solutions were prepared from analytical grade reagents and Millipore Milli-Q ultrapure water (resistivity > 18MΩ cm). Stock solutions of 10^{-3} mol L metal ions were prepared in water and diluted appropriately on the day of use. Experiments were conducted at 25 ± 1°C without deaeration.

Nafion films were prepared according to a previously devised procedure[6]. Briefly, 5 μL of a 0.25% solution of Nafion in ethanol (diluted from a 5 wt% Nafion solution in alcohols and water, Sigma) was applied over the electrode surface, followed immediately by 3 μL of N,N'-dimethylformamide casting solvent. The solvents were evaporated in a warm air stream whilst rotating the electrode slowly for about 1 minute, followed by curing at a temperature of ~70° C for another minute. This led to films of thickness around 1 μm.

Mercury films were prepared by electrodeposition through the Nafion coating within the BIA cell. A volume of 10 μL of a 0.10 mol L^{-1} solution of Hg^{2+} in 0.1 mol L^{-1} KNO$_3$ / 5mmol L^{-1} HNO$_3$ was injected directly over the electrode at an applied potential of –1.0V, this potential being applied for a total of 60 s. This led to closely-spaced mercury microdroplets on the glassy carbon surface and to an array of mercury microelectrodes in the case of the RAM electrode.

BIA-SWASV experiments were carried out using a computer-controlled CV-50W voltammetric analyser (Bioanalytical Systems). In SWASV experiments, the square wave parameters were: frequency 100 Hz, potential increment 2 mV and square wave amplitude 25 mV. These square wave parameters have been previously optimised in order to maximise the stripping signal[5,6]. Metal ions were deposited by injection of a 50 μL sample at 24.5 μL s^{-1} dispension rate using an applied potential of –1.3 V vs SCE during 30 s, pre-concentration continuing after the end of injection for a total of 30 s to maximise electrolysis efficiency[5]. Electrolytes were 0.1 mol L^{-1} KNO$_3$ / 5 mmol L^{-1} HNO$_3$ and 0.1 mol L^{-1} acetate buffer (pH 4.6).

Results and Discussion

Experiments were done with the Nafion-covered mercury thin film electrode (NCMTFE) on the glassy carbon substrate, the RAM-NCMTFE and some experiments at the uncovered MTFE for comparison purposes. Typical voltammetric traces for injection of a mixture of four metal ions at the RAM-NCMTFE are shown in Figure 1. Important characteristics of this voltammetric profile are the sloping background for zinc and copper ions and the differences in stripping peak currents between the various ions, as generally occurs. Although a slower effective scan rate would reduce the background current, at the same time it gives more time for oxygen to diffuse to the electrode surface which also negatively influences the experimental results. The square wave conditions employed were the best compromise. Nevertheless, it was possible to measure these four metal ions in environmental samples as will be shown below.
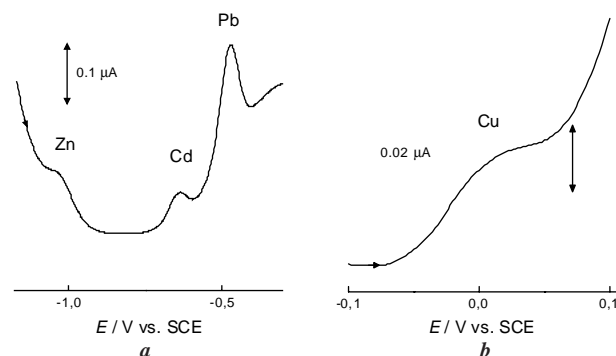
Figure 1. BIA-SWASV voltammogram of (a) Zn^{2+}, Cd^{2+}, Pb^{2+} and (b) Cu^{2+} 10^{-7} mol L^{-1} in 0.10 mol L^{-1} KNO$_3$ / 5mmol L^{-1} HNO$_3$ electrolyte. 50μL injection of mixture of the four ions at the RAM-NCMTFE. E_{dep} = -1.3 V vs SCE; t_{dep} = 30 s.

It was demonstrated at both the NCMTFE and the RAM-NCMTFE that there is virtually no increase in signal on injecting more than 50 μL of sample. The reason is that a large part of the pre-concentration occurs by diffusion after dispension has been completed; for samples of larger volume, convection has caused the first part of the injected sample to reach too far away from the proximity of the electrode(s) to be able to diffuse back, Figure 2. Consequently, to maximise efficiency the lowest dispension rate of 24.5 μL s^{-1} should be used, which was found to be the case.

GLASSY CARBON ELECTRODE SUBSTRATE
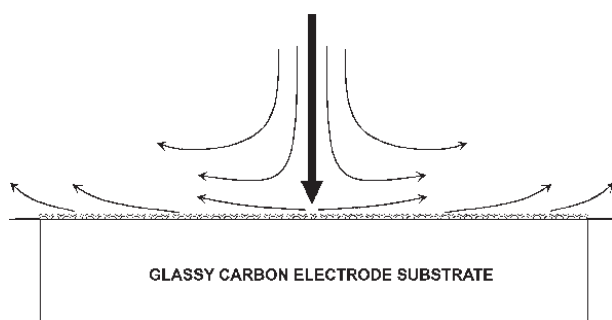
Figure 2. Scheme showing a cross-section of the NCMTFE and the convection profile during injection. The thick arrow shows the incoming jet of solution.

Particular attention was given to lead and cadmium ions in evaluating the characteristics of the assembly for environmental analysis. This was partly to avoid the common difficulties of intermetallic compound formation between copper and zinc in liquid mercury. Typical results are shown in Table 1. Several points can be made. First, linear ranges are up to ~100 nmol L^{-1} in all cases and detection limits (calculated as 3σ) are close to 5 nmol L^{-1}. Secondly, the evident difference in sensitivity for lead and cadmium found at the bare MTFE is further enhanced at the NCMTFE and at the RAM-NCMTFE.

**Table 1.** Determination of lead and cadmium ions by BIA-SWASV at the MTFE, NCMTFE and RAM-NCMTFE

Electrode	Slope (nA nmol L^{-1})	Intercept (μA)	Correlation coefficient
MTFE	Pb 41.0	0.43	0.995 (*n*=5)
	Cd 30.0	0.50	0.995 (*n*=5)
NCMTFE	P 55.0	0.29	0.999 (*n*=5)
	Cd 7.5	0.09	0.999 (*n*=7)
RAM--NCMTFE	Pb 0.91	0.01	0.999 (*n*=5)
	Cd 0.12	0.06	0.995 (*n*=6)

The microelectrode characteristics of RAM electrodes led to a decrease by a factor of at least 1.5 in detection limit, according to the metal ion, and sensitivity as a function of normalised area was higher compared with larger

electrodes. This calculation was based on the geometric areas of the glassy carbon electrode and of the carbon fibres, since both are covered by hemispherical droplets. Further details may be found in[9].

Strategy for environmental analysis

Good discrimination against surfactants - detergents, polyelectrolytes and proteins - has been demonstrated for Nafion films, as exemplified in Figure 3 for cadmium ions. This shows that any stripping signal decrease is not sufficiently large so as to significantly affect the detection limit. For comparison, at a bare MTFE in the absence of the Nafion film, and for a surfactant concentration of 5 mL, the values of ($I_p/I_{p,max}$) decrease to 31% for Triton X-100, 72% for SDS and 81% for protein standard; the values with the Nafion film are 82%, 86% and 94%, respectively. Thus, important benefits arise from coating the electrode with the Nafion film in all cases, particularly so for Triton X-100 detergent.
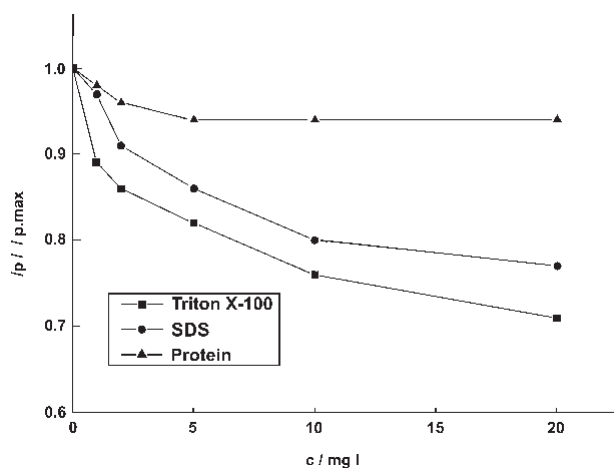
Figure 3. Effect of surfactants on the stripping peak current, I_p, expressed as percentage change with respect to the maximum stripping current $I_{p,max}$ as a function of surfactant concentration. Surfactants Triton X-100 detergent, sodium dodecyl sulphate (SDS) polyelectrolyte, and protein standard (50 gL^{-1} albumin + 30 gL^{-1} globulin - Sigma). Data from BIA-SWASV of cadmium ions at NCMTFE. Other conditions as Figure 1.

An additional potential problem which could arise in applications is due to variations in stripping signal between different coated electrodes[11], which may reach 10%. However, since the standard addition technique is used to determine the levels of these trace metal ions, such differences are unimportant.

Spiking the sample solution also minimises alterations to the sample matrix, and must be used in combination with a strategy for minimisation of the influence of copper-zinc intermetallic compounds and arises from the stability of such compounds in liquid mercury and the fact that the signal for

stripping, i.e. oxidation, of copper-zinc and of copper are virtually coincident on the potential scale. This influence is more evident in mercury thin-film electrodes than in hanging or static mercury drops, owing to the higher concentration of dissolved metals after the pre-concentration step of the anodic stripping voltammetry experiment in the former case. The problem is best resolved by carrying out two consecutive experiments. In the first (deposition potential –1.3V), if a stripping signal at the potential for copper does not appear, then it can be inferred that there is no detectable level of labile copper ion present in the sample. If a signal appears, then a second experiment must be done at a less negative pre-concentration deposition potential, at which zinc ions are not deposited, say –1.0 V, to give the copper level, with no contribution from Cu-Zn. In this second case, by judicious standard addition procedure, the zinc concentration can be inferred by subtracting the copper concentration from the total copper plus zinc concentration. This is simpler than the addition of gallium ions to suppress copper-zinc intermetallic compound formation[12].

Additionally, if clean electrolyte is injected between injections of sample then there is no decrease in response with time. This is due to removal of any potential contaminants from the zone of the electrode surface, as depicted in Figure 2. Apart from the evident convective flow, it can also be explained theoretically by the wall-jet characteristics of the experimental assembly[13] – only solution from the jet of incoming solution can reach the electrode surface by convection.

Environmental analyses

Various samples were collected from clean river water and effluent of industrial origin in an open-air stream, the solutions having a grey aspect in the latter cases. They were kept in polypropylene bottles. The NCMTFE was used for the BIA-SWASV measurements to be described below, although the RAM-NCMTFE was also demonstrated to give good results. Metal ion levels were determined immediately after collection and after digestion in nitric acid for 48 hours at a pH value just below 2. Figure 4 exemplifies the results from three of these samples both in mol L^{-1} and in μg L^{-1}. The reason for the two representations is that, although the electrochemical results are directly related to molar concentrations, toxicity limits are generally specified in terms of w/v, and thus it is easier to compare the latter with the literature. There are noticeable effects on the relative levels if the atomic weights are rather different, as Figure 4 demonstrates. The absence of any bar means that the level of the ion concerned is below the detection limit of 5 nmol L^{-1}.

Two general comments can be made regarding the results obtained. First, in all cases – even visually dirty effluents – the NCMTFE proved to offer excellent protection against blocking by adsorption. Secondly, electrochemical determinations offer the only way to probe the labile fraction of the cations, which should have a reasonable correlation with what can be assimilated by living organisms, plants and animals, and therefore constitutes a toxicity problem[14]. On the timescale and conditions of the SWASV experiment, strong complexes will not be decomposed so that the free cation is reducible.

Specific comments can be made. It can be seen that the amount of labile cation increases after acid digestion. The levels obtained in river water, Figures 4a and 4b, after collection are within the requirements of current legislation, e.g.[15], although this is not the case after acid digestion. The levels measured in the industrial effluent, Figure 4c, do not meet the legislation requirements, particularly regarding zinc.

In river water, the levels of labile lead ions are below the detection limit in the as-collected samples but are easily measured after acid digestion. This is indicative of the destruction of strong complexes formed by the lead cations. The same can be said of the copper cations, Figure 4a.

In the effluent, it is notable that the lead ion concentration diminishes after acid digestion. This rather remarkable fact may be an artefact due to specific interactions of lead cations with detergent-type surfactants in the zone of the electrode surface at neutral pH values and demonstrates the extra care that may need to be taken for measuring lead levels. This interaction can give rise to an increase in lead stripping currents, as has been previously shown[8,11]. Two situations can be envisaged. First, if a large amount of surfactant is present in the sample, then on spiking using the standard addition method the increased pre-concentration effect arising from the interaction between lead cations and detergent molecules should remain unchanged and so the lead stripping signals will increase proportionally with the lead cation concentration. This will lead to a higher sensitivity, but a correct measurement of the lead level in the sample when extrapolation is made to zero stripping current. In the other situation, without excess of surfactant, the enhanced pre-concentration effect will be lessened so that the stripping signal will increase less with increasing added lead concentration, the result being an abnormally high lead determination when extrapolation is made. Nevertheless, despite this problem, there is a rapid-response diagnostic indication that lead is present and that further investigations need to be carried out: ideally the lead level should be zero[15].

The various river water samples show trace metal levels below those permitted for aquatic life by the US Environmental Protection Agency (EPA – 1995)[16].
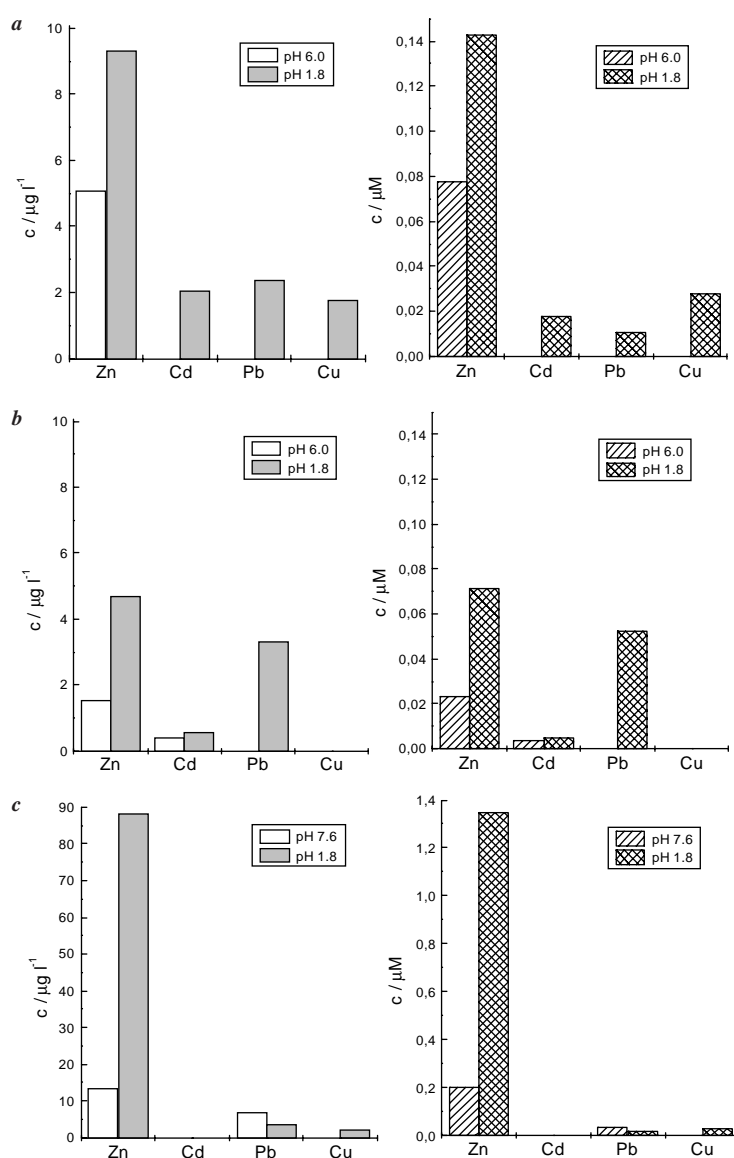
Figure 4. Concentrations of metal ions obtained using BIA-SWASV at the NCMTFE by the standard addition method for as-collected samples (pH ≥6) and after digestion in HNO_3 (48h, pH 1.8). Samples (a) and (b) water from different collection points in river; (c) effluent with large industrial component from open-air stream.

Conclusion

Fast and effective analyses of trace metal ions in environmental samples of natural waters and effluents have been carried out. The results clearly show the advantages of the BIA-SWASV technique at polymer-coated electrodes; the coatings avoid problems of irreversible adsorption leading to blocking and fouling of the electrode surface. The inherent advantages of no pretreatment or necessity of electrolyte addition remove many of the objections for the use of electrochemical methods, which thus have an important role to play in the measurement of the labile fraction of such species in these media. The technique augurs well for real-time on-site analytical determinations.

Acknowledgements

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