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Anodic stripping voltammetry of trace metals by batch injection analysis

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Abstract

The application of batch injection analysis to the determination of trace metals in samples of volume ≤ 100 μl by square wave anodic stripping voltammetry has been investigated in detail, using a programmable electronic micropipette. The in situ formation of a mercury film on a glassy carbon electrode substrate, the influence of preconcentration time, injection rate and injected volume of analyte ions have been studied and optimised procedures are recommended. Results for zinc, cadmium, lead and copper are presented, with particular emphasis on lead and cadmium, and nanomolar detection limits corresponding to sub-picomole quantities found. Comparison is made with flow-injection analysis and with experiments at wall-jet electrodes in continuous flow.

Keywords: Batch injection analysis; Mercury film electrodes; Anodic stripping voltammetry; Trace metals; Flow injection; Cadmium; Copper; Lead; Zinc

1. Introduction

The determination of trace metals is of great environmental concern. Thus there is a continued interest in the procurement of methods which are rapid, require a minimum of sample preparation and can preferably be used either in situ or on-line. Electrochemical detectors in flow systems [1] satisfy many of these criteria, although the consumption of solution is large, unless injection modes are or can be employed. The higher mass transport increases sensitivity and reproducibility and reduces detection limits, but, conversely, a progressive decrease in signal response owing to electrode poisoning during determinations performed in complex solution matrices is also exacerbated by the use of continuous flow systems.

The technique of batch injection analysis (BIA) [2] goes a long way to addressing some of these difficulties. In BIA with electrochemical detection, an aliquot of solution is injected directly above the centre of a disc electrode immersed in electrolyte solution. The disc electrode is usually held at fixed potential so that a current transient is obtained, similar to a flow-injection analysis transient at low rate of dispersion [3], the height of which is proportional to the concentration. Use of a programmable motorised electronic micropipette permits good reproducibility in the transients obtained and several pro-

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gramming modes [4]. Sample volumes injected are on the order of 100 μl or less, often dilution of the analyte sample with electrolyte is unnecessary, electrode poisoning thus being reduced. The wall-jet hydrodynamics [5], in which only the fluid from the fine jet of solution reaches the electrode surface during the injection, means that there are no memory effects – this has been experimentally verified [6].

Further benefits arise through combining BIA with voltammetric detection [7]. First, successive injections during a slow potential sweep permit the construction of a point-by-point pseudo-steady-state voltammetric curve, allowing Tafel analysis and concentration determination from one set of transients. Secondly, cyclic voltammetry can be performed either during or after the injection period. Thirdly, square wave voltammetry can be carried out during the injection. This last benefit permits an increase in sensitivity by a factor of four with respect to fixed-potential amperometric detection and leads to a detection limit of about 5 μmol dm^{-3}.

The combination of BIA and anodic stripping voltammetry (ASV) has been demonstrated, and the general benefits described [8]. However, in these experiments a manual pipette was employed, the mercury film was preformed before introduction of the electrode into the BIA cell, and samples analysed contained metal ions of concentrations on the order of 10–40 ppb (approximately 10^{-7} M), which is too high a limit for some practical applications, for example in the analysis of some mineral waters.

In this paper we explore the full potentialities of the technique, using an electronic micropipette and square wave voltammetric scan in the determination step in order to minimise the problems of dissolved oxygen, etc. and reduce the total time of the experiment. Comparison will be made with similar experiments conducted at the wall-jet electrode [9].

2. Experimental

The entry of a large open wall-jet cell constructed of Perspex and filled with inert electrolyte was modified to hold a micropipette tip (internal tip diameter 0.47 mm) as described previously [6]. This was fixed exactly over the centre of a glassy carbon (Tokai, GC-20) disc electrode at a distance of 2–3 mm, while the cell contained also a platinum gauze counter electrode and a saturated calomel reference electrode.

Injections were performed using a programmable motorised electronic micropipette (EDP Plus 100 EP-100, Rainin). This micropipette, with a maximum dispension volume of 100 μl, has three dispension rates which were calibrated as 24.5, 47.6 and 75.3 μl s^{-1} [6]. Accurate injections of volumes varying between 10 and 100 μl are possible, singly or consecutively, up to a total of 100 μl. Unless specified otherwise, in this work the "MULTIDISPENSE" mode was employed; this mode permits injection without the automatic blow-out and reset step after injection, which occurs in the simplest dispension mode.

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

Solutions were prepared from analytical-reagent grade chemical reagents and Millipore Milli-Q ultrapure water. Experiments were conducted at room temperature (25 ± 1°C) and without deoxygenation. Stock solutions of 10^{-3} M Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} were prepared and diluted on the day of use as appropriate.

3. Results and discussion

A number of parameters in the ASV experiment were examined and the results compared with similar experiments undertaken at the wall-jet electrode. The particular merits which will be addressed are the possible increase in sensitivity resulting from the use of BIA injection of small aliquots of test solution, the detection limits, and simplification of the experimental procedure.

3.1. General strategy

In planning a strategy for these BIA–ASV experiments it is instructive to consider the degree of electrolysis of the injected solution and its maximisation. During the deposition step we can assume wall-jet hydrodynamics, as previously demonstrated [6], and a deposition potential corresponding to the diffusion-limited current. From the wall-jet limiting current equation [5]

$$I_L = 1.59knF\nu^{-5/12}D^{2/3}V_f^{3/4}R^{3/4}a^{-1/2}c_\infty \qquad (1)$$

where k is a constant (0.9), ν is the viscosity of the electrolyte, D the diffusion coefficient of electroactive species of bulk concentration c_∞, V_f the volume flow-rate, a the jet diameter, and R the radius of the electrode, n and F having their usual meaning, and from the expression for the total charge during electrolysis

$$Q = I_L\tau = \eta(I)nFVc_\infty \qquad (2)$$

where V ($= V_f\tau$) is the volume injected, the electrolysis efficiency, $\eta(I)$, is

$$\eta(I) = 1.39\nu^{-5/12}D^{2/3}V_f^{-1/4}R^{3/4}a^{-1/2} \qquad (3)$$

which corresponds, using typical values, to a percentage electrolysis of ca. 0.7% [7]. Since the injection period of the electronic micropipette is of the order of only several seconds, it is therefore important to consider ways of increasing the percentage electrolysis since at the wall-jet and other hydrodynamic electrodes, it would typically be 30 s or more. This result also demonstrates the need for highly discriminative and sensitive instrumental detection modes such as square wave voltammetry.

It has been shown in previous work [10,11] that at the wall-jet radial diffusion begins to play an important role for flow-rates below 0.05 $\text{cm}^3\ \text{s}^{-1}$, which increases the observed current to values above that predicted by Eq. 1. This, in combination with the increase in electrolysis efficiency with decreasing flow-rate, the $V_f^{-1/4}$ dependence in Eq. 3, suggests that the lowest of the three flow-rates should be employed. Secondly, the possibility of increasing the quantity electrolysed by continuing to apply the deposition potential after the injection, this latter deposition occurring through diffusion processes, should be considered. The first of these has been investigated through use of the lower flow-rates, and the second through varying the preconcentration period, as will be discussed below.

3.2. Mercury film formation

The ASV experiment involves the preconcentration of the metal ions to be determined either in a preformed mercury film or in a co-deposited film. In the former case, the electrolyte of choice is usually acidic nitrate medium, the deposition potential being −1.0 V vs. SCE, whereas in the latter case the electrolyte and deposition potential vary according to the procedure. In flow systems, medium exchange can be avoided through co-deposition and use of appropriate protocols for the determination step. Previous work involving co-deposition by ourselves has used sodium perchlorate as supporting electrolyte in experiments at the wall-jet electrode with no medium exchange [9].

Several procedures for mercury film formation were tested using BIA with the three dispension rates and different concentrations of mercury(II). Due to the very small amount of mercury being injected, the normal 10^{-4} M solution of Hg^{2+} (corresponding to 10^{-8} moles for 100 μl assuming 100% electrolysis) would not give a sufficiently good film. Indeed, for pre-deposition at wall-jet electrodes, a solution of 10^{-4} M is usually deposited for several minutes. It was therefore decided to test the injection of 100 μl of more concentrated solutions at the slowest dispension rate (24.5 $\mu\text{l s}^{-1}$) at the beginning of a longer period, of up to 60 s, with −1.0 V applied potential. The integrity of the film was then tested by a background scan and visual inspection.

The experimental conditions for optimum films were background electrolyte 0.10 M KNO_3 + 0.002 M HNO_3, with injection of 100 μl of 0.10 M Hg^{2+}. Mercury films formed were of good thickness and more homogeneous than at the wall-jet electrode where the mercury film thickness falls off with radius, r, as $r^{5/4}$. The reason for this can be traced to the deposition potential being applied at the end of the injection period, which will deposit mercury from the surrounding solution containing mercury ions owing to diffusion. To simplify, the same background electrolyte was used in the cell in further experiments.

This in situ procedure should be contrasted with that previously suggested in [8] where the mercury film was formed by conventional means in a stirred solution elsewhere and the electrode then transferred into the BIA cell. This new protocol is clearly simpler to carry out.

3.3. Effect of square wave parameters

The normal square wave parameters frequency, scan increment and square wave amplitude were varied. As a result of these studies, values of 100 Hz, 2 mV and 25 mV, respectively, were selected. Typical traces are shown in Fig. 1, superimposed on a typical mercury film background. The background is almost horizontal in the region of the cadmium and lead stripping peaks, which means that these elements are easier to analyse quantitatively than zinc and copper under BIA–ASV conditions. Different sensitivities for the four ions are also evident. The effect of the injection parameters and preconcentration (deposition) time will now be discussed.

3.4. Effect of preconcentration time

In previous work [8], it was assumed that ending the preconcentration period directly after the injection, by a manual micropipette in that case, was the best way to achieve highest sensitivity and reproducibility, in analogy to flow-injection analysis. However, the situation in BIA is different since there is no carrier solution. The importance of preconcentration time is demonstrated through the experiment illustrated in Fig. 2a for the ASV of Cd^{2+}. This chronoamperometric transient, similar to that obtained for higher concentrations, shows the maximum deposition current obtained during injection and a decrease in current as soon as injection ends. Whereas for direct measurements without preconcentration at higher concentrations measurements are made at the maximum current [6], stripping voltammetry depends on the total quantity deposited, i.e. the deposition charge. Thus the relaxation part of the transient is of obvious use in increasing sensitivity through further electrolysis of solution remaining in the zone of the electrode after injection. The form of the plot in Fig. 2b confirms this and clearly shows that a maximum value for the current is reached after 60 s, ca. 90% of this value being reached after 20 s. In most of the following experiments a 30-s deposition period was used.

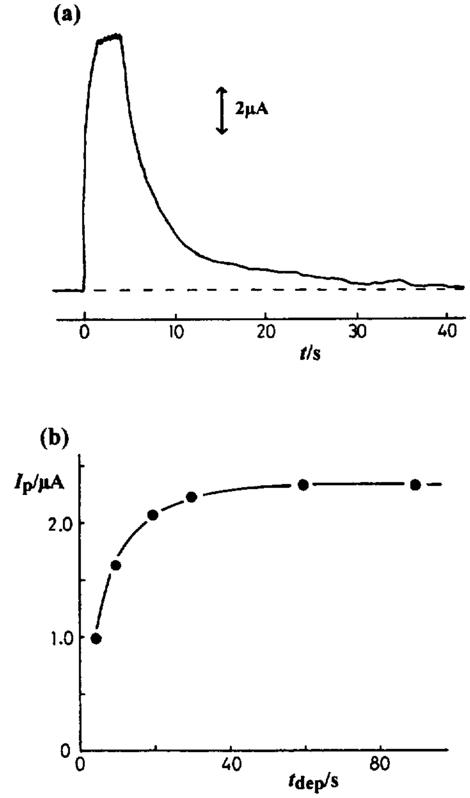

Fig. 2. BIA–ASV of cadmium ($[Cd^{2+}] = 5.0 \times 10^{-8}$ M). (a) Chronoamperometric transient for injection of 100 μl at 24.5 μl s^{-1}, $E = -1.0$ V vs. SCE. (b) Effect of preconcentration time on peak current, I_p, in BIA–ASV; experimental parameters as in Fig. 1.

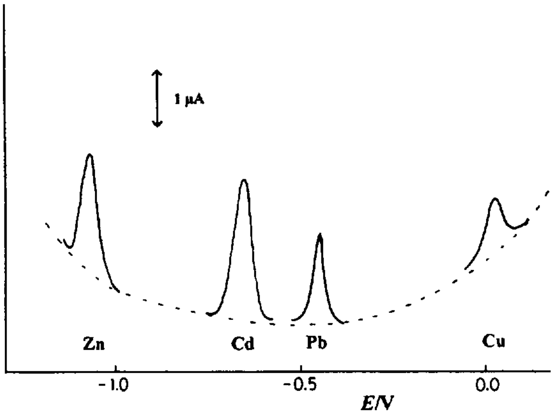

Fig. 1. Typical traces for BIA–ASV of Zn, Cd and Pb and Cu from solutions of 5×10^{-8} M in 0.1 M KNO_3–0.002 M HNO_3 and measured separately. 50 μl injection at 24.5 μl s^{-1}, deposition time 30 s at -1.3 V vs. SCE. Square wave parameters: 25 mV amplitude, scan increment 2 mV, frequency 100 Hz. Dotted line shows typical mercury film background.

3.5. Effect of injected volume

In a continuous flow system the peak height recorded is a linear function of the volume of analyte

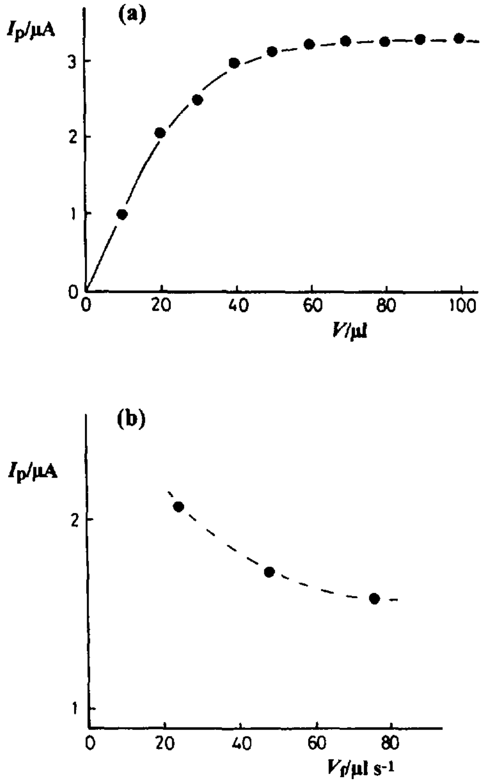

Fig. 3. (a) Effect of injection volume, V, on peak current, I_p, in BIA–ASV of lead ($[Pb^{2+}] = 1.0 \times 10^{-7}$ M); other parameters as in Fig. 1. (b) Effect of flow-rate on peak current in BIA–ASV of lead ($[Pb^{2+}] = 1.0 \times 10^{-7}$ M); other parameters as in Fig. 1, except $t_{dep} = 5$ s.

which passes the detector. However, although a dependence on the injected volume was found, it is not a linear relation for BIA–ASV as shown in Fig. 3a, except for cases when the deposition potential was ceased to be applied immediately after injection. This general dependence can therefore be attributed to the fact that some injection solution pushed far from the electrode cannot reach the electrode surface during the post-injection deposition period. For this reason, an injection volume of 50 μl is adequate.

3.6. Effect of injection rate

The dependence on injection rate is predicted from Eqs. 2 and 3 to be proportional to $V_f^{-1/4}$. The points in Fig. 3b correspond to a proportionality exponent of approximately -0.3 from high to low flow-rates, respectively, determined from the expression for the peak current, I_p

$$I_p = pV_f^{-x} \tag{4}$$

or

$$\log I_p = -x \log V_f + \log p \tag{5}$$

where $-x$ is the exponent and p embraces all the other terms which are held constant. Consideration of the radial diffusion effects, as discussed above, can assist in explaining the slightly higher than predicted exponent. Additionally, the diffusion that occurs after the injection period itself increases the signal, so that after 30 s preconcentration the difference between the peak currents is much smaller (not shown). Nevertheless, the general conclusion remains that the lowest flow-rate should be employed.

This led us to investigate the "TITRATE" mode in the micropipette. This mode dispenses the liquid in a succession of tiny jets, the interval at an increasing rate if the trigger is held. Releasing the trigger and starting again returns to the slow rate. It thus dispenses the liquid more slowly than normal dispension, but in a less reproducible manner. Comparison with the lowest injection rate in "MULTIDISPENSE" mode leads to peak currents of the same height if time is left between each trigger action. Therefore this mode offers no benefits in terms of increased percentage electrolysis; the reason is probably the on–off characteristic of the convective flow, which may lead to turbulence and the electroactive species not reaching the electrode surface.

3.7. Calibration plots

Typical calibration plots for the determination of cadmium and lead separately are shown in Fig. 4. Linear regression leads to a slope of 0.039 μA nM^{-1}, intercept 0.41 μA, with regression coefficient 99.8% for cadmium and a slope of 0.025 μA nM^{-1}, intercept 0.55 μA with regression coefficient 99.2% for lead. As verified from examination of the plots and the less good linearity at low concentrations, practical detection limits are on the order of 2–3 nM; the linear range extends to 10^{-6} M. Comparison with [8] reveals that the new experimental protocol developed here leads to higher sensitivities and, consequently, lower detection limits.

It is not clear at present why there should be an intercept in the calibration plots, but it becomes relatively unimportant for analyte concentrations on the order of 10^{-7} M. A possible reason for its occurrence is carry-over effects. It was found that there is no memory effect in non-pre-concentration batch injection experiments, due to the wall-jet hydrodynamic profile [6]. With the mercury film, to attempt to ensure that no metal ions from the previous experiment in the solution at the mercury film surface or non-oxidised metal can be reduced before or at the beginning of the deposition period, an injection of electrolyte was done at an applied potential of 0 V when all species were oxidised. In this way, very good reproducibility between successive injections of the same concentration was obtained and the intercepts reduced to the values shown, but it was not possible to remove them entirely.

In mixtures of lead and cadmium ions the slopes of the calibration plots differ slightly from those obtained by analysing solutions containing the ions separately: for cadmium 0.042 μA nM^{-1} with intercept 0.206 μA, regression coefficient 99.8% and for lead 0.023 μA nM^{-1} with intercept 0.413 μA, regression coefficient 99.8%. Such differences have been encountered in ASV experiments at wall-jet electrodes [9] and will be discussed further below.

Thus, the analysis of practical samples can be divided into two categories: samples with metal concentration on the order of 10^{-7} M and those with metal concentration less than this. In the first case the intercept can be taken as zero and either a one- or two-point calibration curve is constructed or the standard addition method is used. In the latter case, a two-point calibration curve needs to be constructed, and the standard addition method is less recommended, although it may still be important for mixtures. In Fig. 5 is shown the trace obtained for a diluted wastewater containing a mixture of zinc, cadmium, lead and copper. Analysis of this curve showed that the sample contains 3×10^{-8} M (2 μg dm^{-3}) zinc, 1×10^{-7} M (11 μg dm^{-3}) cadmium, 3×10^{-7} M (60 μg dm^{-3}) lead and 2×10^{-8} M (1.2 μg dm^{-3}) copper.

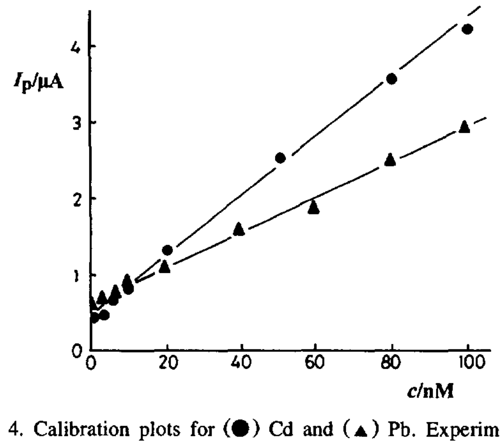

Fig. 4. Calibration plots for (●) Cd and (▲) Pb. Experimental conditions as in Fig. 1.

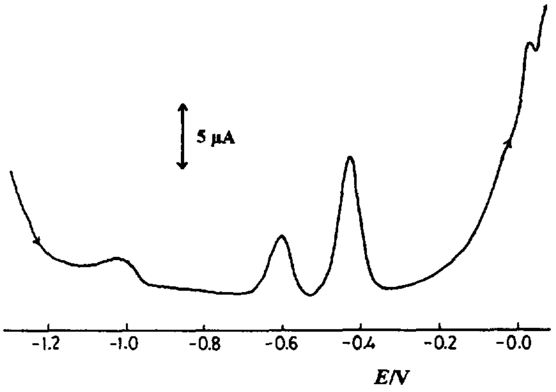

Fig. 5. Experimental BIA–ASV trace for diluted wastewater analysis.

3.8. Comparison with flow-injection analysis

In flow-injection analysis a sample is injected into a carrier stream and flows past the detector. Under comparable experimental conditions, similar precision and sensitivity are to be expected; however, this will not usually be the case because of differences in experimental protocols. There are several main differences between BIA–ASV and its flow-injection analogue. First, there is no need for a carrier stream with commutators to change the flow stream from mercury deposition to the ASV experiment, which leads to simplification of the experimental procedure. Secondly, in many cases the thickness of the region containing sample solution compared to the distance between working and counter electrodes in BIA is small, leading to low ohmic drop even without added electrolyte – this situation is not easy to achieve in FIA. Thirdly, there is an increased sensitivity and lower detection limit in BIA–ASV due to the continuation of the deposition period after injection has been completed.

3.9. Comparison with wall-jet electrodes

Comparison of these results can be done with a recent study undertaken on the ASV of cadmium and lead at the wall-jet electrode [9]. The comparison will be done with determinations made under optimised experimental conditions, which are clearly different for each case, but correspond to those to be used in practice. In this work a slope of 0.039 μA nM^{-1} was found for cadmium and 0.025 μA nM^{-1} for lead in the calibration curve, these values becoming 0.042 and 0.023, respectively, in the mixture. Optimised conditions at the wall-jet electrode (120 s deposition, square wave amplitude 50 mV at 100 Hz, 2 mV scan increment, flow-rate 45 μl s^{-1}) led to 5.2 and 3.2 μA nM^{-1} for cadmium and lead when analysed separately and 6.6 and 2.9 μA nM^{-1} in the mixture. Thus the increase in the cadmium slope and decrease in the lead slope occur in both cases, although not so much in the BIA experiments. Nevertheless, the difference in sensitivity between wall-jet ASV and BIA–ASV is on the order of a factor of one hundred. This is explained principally through the lower deposition time. In the wall-jet case, the stripping is done in flowing solution which alters the shape of the stripping voltammetric profile, causing it to be sharper, and can lead to a greater peak height.

Thus, the wall-jet system in continuous flow offers higher sensitivities, although the detection limit attainable in practice (ca. 1 nM) is not appreciably lower than for BIA–ASV. BIA offers clear benefits in situations where only small volumes of sample are available, for example in applications to biological fluids.

4. Conclusions

This work has shown how the merits of batch injection analysis can be fully exploited in anodic stripping voltammetry, and comparison has been made with wall-jet electrodes in continuous flow systems. The influence of injection volume and injection rate have been studied. Increased sensitivity arising from continuing to apply the deposition potential after the end of the injection period has been demonstrated. Using optimised experimental strategies, detection limits on the order of several nanomolar, corresponding to sub-picomole quantities for the microlitre volumes injected, have been found. Further work will address the use of BIA for adsorptive stripping voltammetry and enhancement of the discrimination against contamination from adsorption on the electrode in complex matrices through suitable electrode modification procedures.

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References

[1] K. Stulik and V. Pacakova, Electroanalytical Measurements in Flowing Liquids, Ellis Horwood, Chichester, 1987.
[2] J. Wang and Z. Taha, Anal. Chem., 63 (1991) 1053.
[3] J. Wang, Microchem. J., 45 (1992) 219.
[4] J. Wang, L. Chen, L. Angnes and B. Tian, Anal. Chim. Acta, 267 (1992) 171.
[5] C.M.A. Brett and A.M. Oliveira Brett, Electrochemistry. Principles, Methods and Applications, Oxford University Press, Oxford, 1993, Chap. 8.
[6] C.M.A. Brett, A.M. Oliveira Brett and L. Costel Mitoseriu, Electroanalysis, 7 (1995) 225.
[7] C.M.A. Brett, A.M. Oliveira Brett and L. Costel Mitoseriu, Anal. Chem., 66 (1994) 3145.
[8] J. Wang, J. Lu and L. Chen, Anal. Chim. Acta, 259 (1992) 123.
[9] C.M.A. Brett, J.L.C. Lima and M.B. Quinaz Garcia, Analyst, 119 (1994) 1229.
[10] C.M.A. Brett, A.M., Oliveira Brett, A.C. Fisher and R.G. Compton, J. Electroanal. Chem., 334 (1992) 57.
[11] R.G. Compton, A.C. Fisher, M.H. Latham, R.G. Wellington, C.M.A. Brett and A.M. Oliveira Brett, J. Appl. Electrochem., 23 (1993) 98.