

Batch Injection Analysis with Adsorptive Stripping Voltammetry for the Determination of Traces of Nickel and Cobalt

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Abstract

Square wave adsorptive stripping voltammetry (AdSV) in conjunction with the batch injection analysis technique has been investigated at mercury thin-film electrodes, using analysis of nickel and cobalt ions with nioxime ligand as example, and injection of sample volumes of $\leq 100 \mu\text{L}$. Experiments were conducted in a HEPES neutral buffered medium, suitable for analysis of biological fluids. Sensitivity is maximized by continuing the adsorptive accumulation after the end of the injection period, and employing the lowest possible injection rate from the electronic micropipette of $24.5 \mu\text{L s}^{-1}$. The practical detection limit is 5 nM for nickel and 2 nM for cobalt. Comparison is made with batch injection analysis with anodic stripping voltammetry and the merits of the technique relative to continuous flow-through methods are assessed.

Keywords: Batch injection analysis, Mercury thin film electrodes, Adsorptive stripping voltammetry, Trace metals, Nickel and cobalt determination

1. Introduction

The batch injection analysis (BIA) technique [1] with electrochemical amperometric [2] and voltammetric [3] detection of small ($\leq 100 \mu\text{L}$) volumes of liquid samples injected from an electronic, motorized micropipette has been the subject of recent thorough investigation [2,3] and shows similarities with wall-jet systems in continuous flow. Besides its simplicity and requiring only μL volumes of analyte, the contact time between sample and electrode is small which can be of benefit in the analysis of samples in complex matrices, where there is a tendency for electrode fouling to occur. Compared with flow injection analysis [4], in BIA there is no carrier solution with commutators to change the flow stream, which simplifies the experimental set-up, instead it being necessary merely to inject different analyte samples, since the memory effects are zero or close to zero.

Further work has combined BIA with the anodic stripping voltammetry of zinc, cadmium, lead and copper using square wave voltammetry in the determination step [5,6]. It has been shown [6] that nanomolar detection limits are possible with the injection of only $50 \mu\text{L}$ of sample solution onto a mercury thin film electrode prepared *in situ* by injection of a mercury solution onto a glassy carbon substrate. Optimum conditions for the determination were investigated and mixtures analyzed. It was found advantageous in mercury film formation and for maximizing sensitivity in all ASV experiments to continue to apply the preconcentration for periods of up to at least 30 s, enabling the relevant species remaining in solution close to the electrode after the injection period, which lasts for up to 4 s, to reach the electrode surface by diffusion. It was found best to use the lowest of the three possible flow rates. Also, for long preconcentration times, little signal enhancement was gained by using injected volumes greater than $50 \mu\text{L}$ since a large contribution to the amount deposited was obtained by diffusion after the end of the injection when, for larger volumes, the first part of the injected sample was too far from the electrode to contribute to the diffusion.

An interesting potential application of BIA is its use in combination with adsorptive stripping voltammetry (AdSV). The AdSV of cobalt and nickel has been the subject of a number

of studies, usually employing oxime ligands which are highly specific for the divalent ions of these metals [7]. While most work was at a hanging mercury drop electrode (HMDE), e.g. [8,9], more recently it has been demonstrated that it is possible to perform differential pulse AdSV at mercury thin film electrodes in flowing solution, specifically at wall-jet electrodes [10]. The complexes are adsorbed on the mercury surface and then reduced in the determination step. It was shown through impedance measurements [10] that the adsorption mechanism involves exchange of the metal ions from complexes in solution to ligands already adsorbed on the mercury surface.

Square wave adsorptive stripping voltammetry (SWAdSV) was shown to be a viable alternative to differential pulse AdSV at the HMDE [11,12]. Recently, SWAdSV at a rotating mercury thin film electrode was demonstrated to have higher sensitivity than differential pulse AdSV under the same experimental conditions for the determination of nickel and copper [13].

The objective of this study was to apply and adapt the wall-jet procedure described in [10] to batch injection analysis. In [10] it was found more advantageous to employ nioxime (1,2-cyclohexanedione dioxime) ligand than the usual dimethylglyoxime since higher current sensitivities were found. The optimum electrolyte was 0.1 M NaClO_4 + 30 mM HEPES buffer (pH 7.4), given the potential applications to analysis of biological fluids, and the fact that ammonia buffer caused practical problems related to gas evolution in the flow system. In [10], differential pulse voltammetry was employed in the determination step, now replaced with a square wave voltammetric scan.

2. Experimental

The large open wall-jet cell modified for BIA, constructed of Perspex and filled with inert electrolyte was as described previously [2]. The micropipette tip (internal tip diameter 0.47 mm) was fixed exactly over the center of a glassy carbon (Tokai, GC-20) disk electrode at a distance of 2–3 mm. A platinum gauze counter electrode and a saturated calomel reference electrode were also placed in the cell.

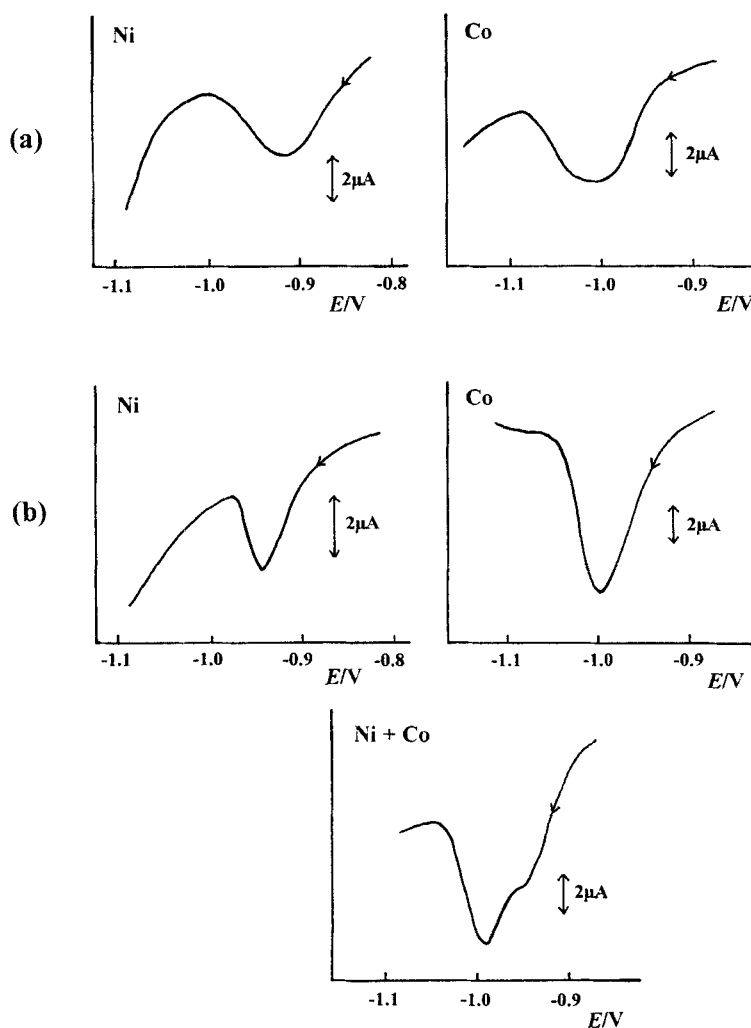


Fig. 1 Typical AdSV square wave voltammograms from reduction of nioxime complexes of Ni and Co following injection of $100\ \mu\text{L}$ at $-0.7\ \text{V}$ (vs. SCE) at flow rate $24.5\ \mu\text{L s}^{-1}$ and adsorption accumulation for 120 s. Injected solution: $[\text{Ni}^{2+}] = [\text{Co}^{2+}] = 1.0 \times 10^{-7}\ \text{M}$; $[\text{nioxime}] = 10^{-4}\ \text{M}$. Square wave parameters: frequency 25 Hz, scan increment 2 mV, pulse amplitude 25 mV. Injected solutions prepared in: a) 0.1 M KNO_3 electrolyte; b) 0.1 M HEPES electrolyte.

Injections were performed using a programmable motorized electronic micropipette (EDP Plus 100 EP-100, Rainin Instrument Co. Inc.). This micropipette, of maximum dispensation volume $100\ \mu\text{L}$, has three dispensation rates which were calibrated as 24.5, 47.6 and $75.3\ \mu\text{L s}^{-1}$ [2], and was employed in the multidispense mode.

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. Nioxime (1,2-cyclohexanedione dioxime) and HEPES buffer (hemisodium salt of *N*-[2-hydroxyethyl] piperazine-*N'*-[2-ethane-sulfonic acid]) were obtained from Sigma Chemical Co. (Poole, Dorset, UK) and used as received. Experiments were conducted at room temperature ($25 \pm 1^\circ\text{C}$) and without deoxygenation. Stock solutions of $4 \times 10^{-3}\ \text{M}$ nioxime and $10^{-3}\ \text{M}$ Co^{2+} and Ni^{2+} were prepared and diluted and mixed on the day as appropriate.

3. Results and Discussion

The initial experimental protocols used were similar to those determined for BIA with anodic stripping voltammetry [6]. In

particular, mercury film formation was done in a similar way as previously by injection from the micropipette, and preconcentration times longer than the injection period were used. The mercury film was prepared on the glassy carbon substrate by injection of $100\ \mu\text{L}$ of a solution of $0.1\ \text{M}$ Hg^{2+} in $0.1\ \text{M}$ KNO_3 solution in the BIA cell at the lowest dispensation rate, $24.5\ \mu\text{L s}^{-1}$, during application of a potential of $-1.0\ \text{V}$ (vs. SCE) for 30 s. Nevertheless, the electrolyte for performing the AdSV experiment itself needed to be investigated and will be discussed below. The investigation of a number of other relevant parameters will also be described.

3.1. Mercury Thin Film and Electrolyte

Besides the procedure for mercury thin film formation in nitrate medium mentioned above, which has been shown to be successful, injection in HEPES electrolyte, a biological buffer, to be used for the metal ion injections, was also investigated. In this case $0.1\ \text{M}$ HEPES was employed, rather than the $30\ \text{mM}$ HEPES/ $0.1\ \text{M}$ NaClO_4 mixture in previous work at the wall-jet [10]. Voltammograms of the mercury film after its formation and visual inspection showed that both procedures were equally good.

The nitrate (pH 4.7) and HEPES (pH 7.4) media were also used for the injection of cobalt and nickel analytes. The general

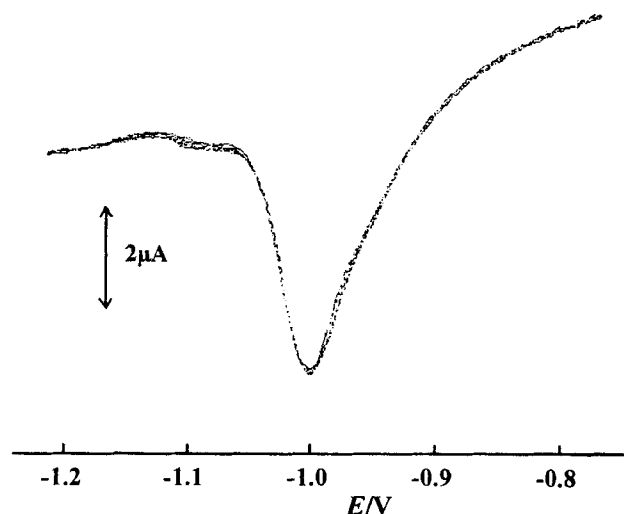


Fig. 2 Five successive determinations of cobalt by BIA-AdSV ($[Co^{2+}] = 5.0 \times 10^{-8} M$). Other conditions as Figure 1b.

experimental protocol followed that used at wall-jet electrodes, i.e. adsorption-accumulation of the complexes at $-0.7 V$ (vs. SCE) followed by a scan in the determination step to $-1.3 V$. It was found advantageous, by judicious addition of small aliquots of the ligand stock solution, to mix ligand with the cobalt and nickel solutions before injection such that the final ligand concentration was $10^{-4} M$, so that the complexes were already formed in solution. Figure 1 shows typical injections for Co and Ni in the two electrolyte solutions. As can be readily ascertained, the results in HEPES medium are superior to those in nitrate medium, particularly regarding peak width. In these better conditions, the Ni peak appears at $-0.94 V$ and the Co peak at $-1.00 V$ (vs. SCE). Nevertheless, in mixtures the two peaks are affected and there is some mutual interference and overlapping (Fig. 1b). Broadening is due partly to kinetic limitations appearing in the square wave voltammetry response in the determination step (see below). Peak width is greater than in DPAdSV. Use of different ligands and buffers may reduce the peak width and overlap. However, the conventional ammonia buffer with dimethylglyoxime ligand [8] is not necessarily convenient for analysis of biological analytes. Another approach in mixtures is to apply deconvolution procedures through curve-fitting as described in [14].

The square wave parameters were investigated. In contrast to BIA-ASV described previously [6], effects of electrode kinetics appear in the square wave response. Therefore the optimum square wave frequency is lower at 25 Hz, rather than 100 Hz, in order to obtain a good peak response. Best reproducibility, demonstrated in Figure 2, was obtained by conditioning the electrode at a potential of $-0.3 V$ for 1 min and washing the electrode by injection of electrolyte (without ligand) between each determination (RSD between determinations is 1.5%). There are some carry-over effects if this is not done, which is to be expected given the easy formation of complexes on the electrode surface.

3.2. Adsorption Time

The effect of adsorption time on the peak current in the determination step is shown in Figure 3a. This demonstrates, as was found with BIA-anodic stripping voltammetry [6], that the continuing adsorption after the end of the injection period itself through diffusion processes is crucial in maximizing the current response in the determination step. In fact, a maximum peak

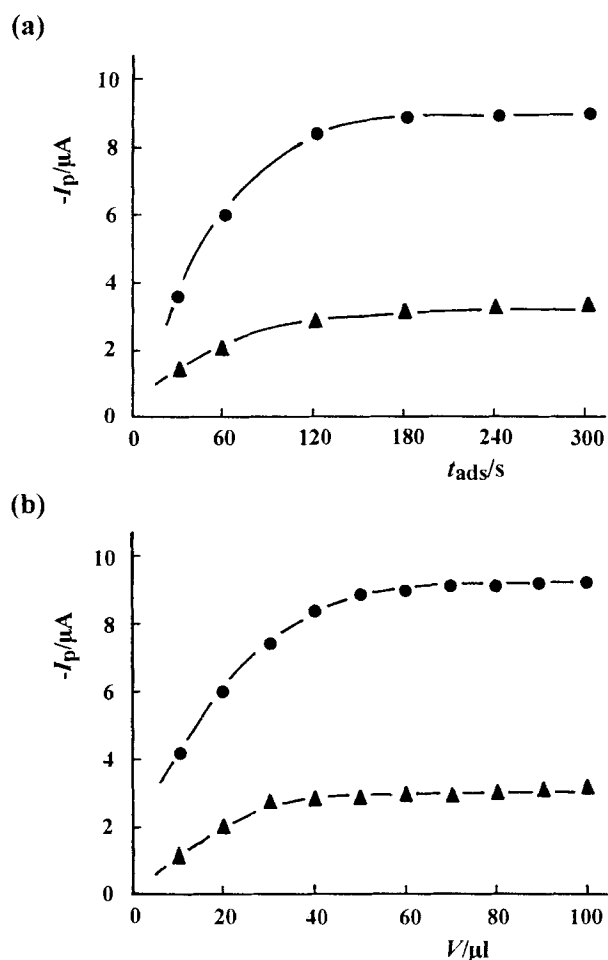


Fig. 3 Influence on reduction peak current, I_p , for Ni (▲) and Co (●) of (a) adsorption accumulation time, t_{ads} , for injection of $100 \mu L$ Co or Ni and (b) injected volume, V , for $t_{ads} = 120 s$. Other conditions as Figure 1b.

current is reached after approximately 120 s preconcentration, whereas for BIA-ASV it was reached after 30 s [6]. This increased time can be explained through the different nature of the preconcentration processes: in the AdSV case a maximum response will be reached after equilibrium between adsorbed and desorbed complexes has been attained. It was also verified that the variation of the normalized peak current with adsorption time is essentially concentration-independent, and that greatest sensitivity is obtained at the lowest dispersion rate of $24.5 \mu L s^{-1}$.

3.3. Injection Volume

The influence of injection volume is similar to that found for ASV, see Figure 3b, i.e., an injected volume of $50 \mu L$ is sufficient to reach the maximum current, a consequence of the diffusion processes occurring after the injection period. Note also the clearly higher currents for cobalt than for nickel due to catalytic cycling effects between $Co^{(I)}$ and $Co^{(II)}$, which is commonly found. The factor increase for the cobalt signal relative to that of nickel is approximately 3, as compared to 2 in continuous flow differential pulse AdSV at the wall-jet electrode [7].

3.4. Calibration Plots

In Figure 4 are shown calibration plots for nickel and cobalt. As can be seen, a good straight line is obtained in these plots

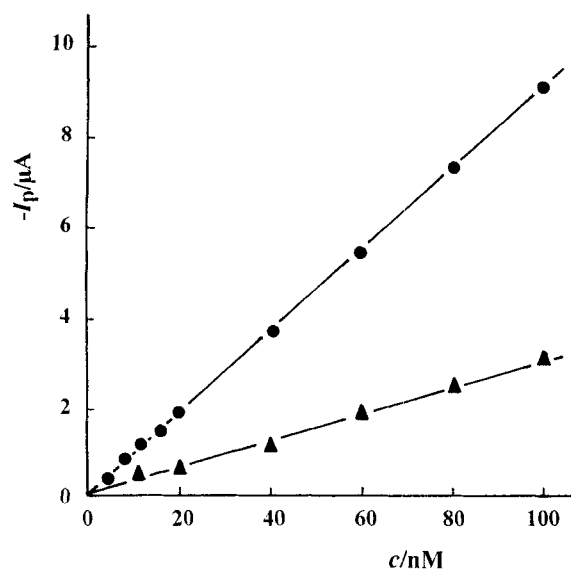


Fig. 4 Calibration plots for Ni (▲) and Co (●). Other conditions as Figure 1b.

with slopes of $0.092 \mu\text{A}/\text{nM}$ and $0.030 \mu\text{A}/\text{nM}$ for cobalt and nickel respectively. This should be compared with values of $0.17 \mu\text{A}/\text{nM}$ and $0.08 \mu\text{A}/\text{nM}$ at the wall-jet electrode in continuous flow with differential pulse AdSV under optimized conditions of flow rate $0.034 \text{ cm}^3 \text{ s}^{-1}$ and adsorption time 60 s [7]. At first sight, these similar sensitivities are surprising. However, the effect of continuing adsorption after injection increasing the signal, as discussed above and in Figure 3a, and the greater sensitivity of square wave over differential pulse voltammetry, can explain this result. Practical detection limits in the nanomolar concentration range (5 nM for nickel and 2 nM for cobalt with RSD 3% for 5 determinations in both cases) corresponding, respectively, to 0.5 and 0.2 pmol for $100 \mu\text{L}$ injections. Good zero intercepts are obtained; in this sense, the technique works better than for BIA-ASV [5] where intercepts were obtained. From signal/noise considerations, a theoretical detection limit of $5 \times 10^{-11} \text{ M}$ is obtained. As would be predicted, there is no evidence of mercury electrode surface saturation effects at long preconcentration times as obtained in continuous flow systems [7].

For analyte solutions containing both nickel and cobalt ions, as is evident from Figure 1c, there is significant overlap between the nickel and cobalt signals such that a simple measurement of peak heights leads to a smaller cobalt signal than predicted and a larger nickel signal. Nevertheless, and despite this, good straight line calibration plots are obtained (not shown) but for accurate values a proper deconvolution procedure needs to be utilized, such as described in [14]. Thus, mixtures of cobalt and nickel are less easy to analyze by this technique than the metal ions separately. This limitation should be born in mind when applying the technique to biological fluids, and may be partially solved by the use of another type of oxime or other ligand, or the curve fitting procedures referred to above.

4. Conclusions

It has been shown that the technique of batch injection analysis can be applied to adsorptive stripping voltammetry, using as example the determination of traces of nickel and cobalt at nanomolar (sub-ppb) levels through adsorption as nioxime complexes on mercury thin-film electrodes. General merits with respect to AdSV in continuous flow arise from the small sample volume of $50\text{--}100 \mu\text{L}$ and the simplicity of the experimental set-up. In relation to FIA-AdSV procedures, besides the advantages of BIA vs. FIA referred to in the introduction and assuming equal volumes are injected, there is the extra sensitivity obtained in the BIA procedure through continued accumulation by diffusion after the end of the injection period.

It is to be expected that BIA-AdSV can be easily extended to other metal-ligand systems through adaptation of previously developed adsorptive stripping voltammetric procedures. It will be especially useful where the amount of sample available is small and results are needed quickly with a minimum of complication.

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6. References

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