

**ELECTROANALYSIS OF TRACES OF COBALT AND NICKEL AT WALL-JET
ELECTRODES IN FLOWING SOLUTION**

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ABSTRACT

The square wave adsorptive stripping voltammetry of cobalt and nickel has been investigated at a wall-jet mercury thin film disc electrode in continuous flow. Following a study of the stripping response, experimental parameters were optimised and a sensitivity enhancement of an order of magnitude over similar differential pulse procedures was found. Applications are discussed.

KEYWORDS: cobalt, nickel, wall-jet electrodes, continuous flow, trace analysis

INTRODUCTION

The measurement of trace, sub-ppb, levels of cobalt and nickel has become important since, although they are essential elements, variations in the small quantities necessary can lead to deficiency or toxicity problems. Cobalt is an essential element and is a constituent of vitamin B12. Its toxicity is usually associated with cardiomyopathy and excessive consumption of beer, to which cobalt is added to increase its qualities. Nickel is much used in jewellery which can result in skin problems; additionally, it is suspected that, besides other carcinogenic compounds, the nickel in cigarette smoke also has a carcinogenic effect on the respiratory pathways and on the lungs [1].

Both cobalt and nickel can be determined electrochemically by adsorptive stripping voltammetry via the formation of complexes with oximes. These oxime complexes are accumulated on the surface of a mercury electrode at an appropriate applied negative potential and are then reduced in the determination step, by a potential scan in the negative direction. This general procedure was originally described at the hanging mercury drop electrode using dimethylglyoxime complexes in ammonia buffer and a differential pulse voltammetric scan in the determination step [2]. Since then procedures have been developed at mercury thin-film electrodes on solid substrates, and significantly in continuously flowing solution [3]. In the latter a wall-jet electrode cell was employed and nioxime (1,2-cyclohexanedione-dioxime) complexes were formed on the mercury electrode surface in pH 7.4 HEPES biological buffer with 0.1M sodium perchlorate electrolyte. Advantages of using nioxime arise from its higher solubility in water than dimethylglyoxime [4].

In order to take maximum advantage from fast instrumental techniques together with the increase in mass transport arising from flowing solution, the square wave adsorptive stripping voltammetry of cobalt and nickel has been investigated and developed at a wall-jet mercury thin film disc electrode

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in continuous flow. Square wave voltammetric scans are faster than differential pulse scans, often leading to higher practical sensitivities, and solution deoxygenation usually becomes unnecessary, leading to significant savings in time. After a study of the stripping waveforms, experimental parameters were evaluated and optimised: solution flow rate, square wave parameters and adsorption time.

EXPERIMENTAL

The wall-jet cell, of the type described in [5], contained a glassy carbon disc working electrode, diameter 0.30 cm, a Ag/AgCl (3.0M KCl) reference electrode in a separate compartment, and a platinum tube auxiliary electrode in the cell outlet. The inlet nozzle diameter was 0.34 mm. Solution was pumped through the cell using a Gilson Minipuls 3 peristaltic pump following damping of solution flow oscillations, usually at a flow rate of $0.035 \text{ cm}^3 \text{ s}^{-1}$. An Eco-Chemie PSTAT10 Autolab potentiostat was used to control experiments and analyse the current response.

Solutions were prepared from analytical grade reagents and ultrapure water. Experiments were done at room temperature ($\pm 23^\circ\text{C}$) without sample deoxygenation.

Mercury films were pre-formed on the glassy carbon electrode substrate from a solution of 10^{-4}M Hg^{2+} in acidified nitrate electrolyte, 5mM HNO_3 in 0.1M KNO_3 , within the wall-jet cell, by electrodeposition at -1.0V vs. Ag/AgCl during 300s. The flow of solution through the wall-jet cell was then changed to that containing the cations cobalt and nickel and nioxime by means of a commutator valve.

Adsorptive stripping voltammetry experiments were carried out in 30mM HEPES + 0.1 M sodium perchlorate electrolyte, pH 7.4, with 1.0×10^{-4} M nioxime, by adsorption at -0.7V vs. Ag/AgCl for a time t_{ads} , followed by a square wave voltammetric scan from this potential in the negative direction until -1.2V.

RESULTS AND DISCUSSION

Asymmetric square wave reduction peaks for cobalt and nickel were obtained, see Fig.1, the heights of which are altered slightly in mixtures. The peak potential for nickel is at -0.925 V and that for cobalt at -1.005 V. Analysis of the forward and reverse square wave currents confirmed this to be due to strong adsorption of the complex at the mercury/solution interface [6], in that the reverse response was very small. The ratio of cobalt to nickel peak current of nearly two suggests catalytic effects: this has been observed previously by various authors [3,7] and is generally attributed to cycling between the Co(I) and Co(II) oxidation states. There is sufficient peak separation for quantitative analysis.

Various experiments were carried out to determine the best experimental conditions for quantitative analysis. Fig.2 shows the variation of peak potential with square wave frequency, f , and with square wave amplitude, h . The variation of peak current with these parameters led to best values of 100Hz and 30mV respectively, as a compromise between increasing current and some increase in peak width due to kinetic effects.

Regarding the flow rate, it was previously shown [8] that the response increases with flow rate up to approximately $0.035 \text{ cm}^3 \text{ s}^{-1}$; for higher flow rates the response does not alter further. This was explained [8] through the reduced diffusion layer, the thickness of which becomes sufficiently thin so as not to allow the equilibrium for adsorption/desorption of the complexes to occur under natural conditions during the accumulation step. Thus a flow rate of $0.035 \text{ cm}^3 \text{ s}^{-1}$ was used for all experiments described.

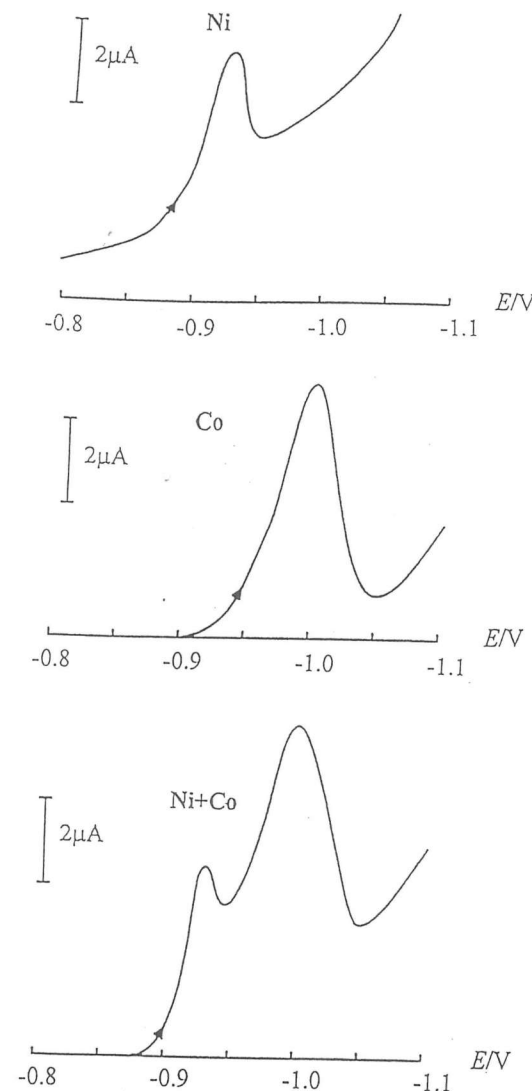
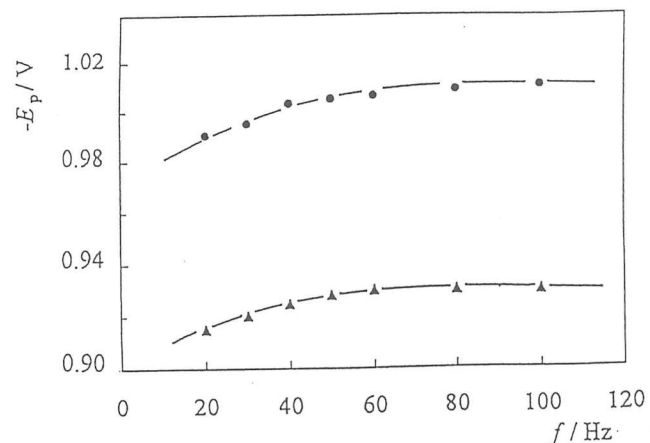


Fig.1 Typical traces from SWAdSV of cobalt and nickel at the wall-jet mercury thin-film electrode, separately and as a mixture. Experimental conditions: $V_r = 0.035 \text{ cm}^3 \text{ s}^{-1}$, $t_{\text{ads}} = 60\text{s}$, $f = 40\text{Hz}$, $\Delta E_s = 2\text{mV}$, $[\text{M}^{2+}] = 1.0 \times 10^{-8} \text{ mol dm}^{-3}$.

a)



b)

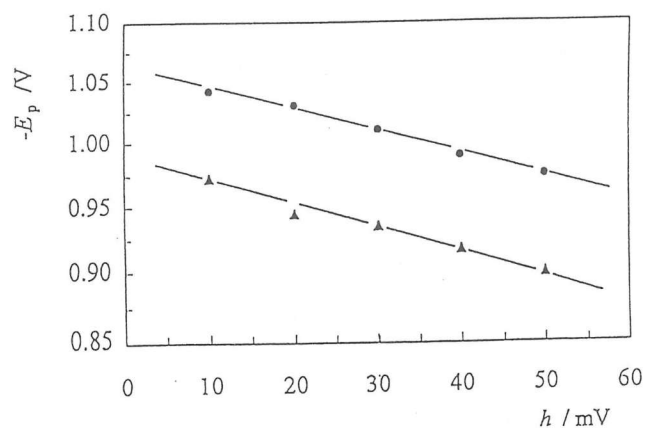


Fig.2 Effect on the value of the SWAdSV peak potential of (a) square wave frequency [Co^{2+}] = [Ni^{2+}] = 6.0×10^{-9} mol dm⁻³ (b) square wave amplitude ($f = 100$ Hz, [Co^{2+}] = [Ni^{2+}] = 8.0×10^{-9} mol dm⁻³). Other conditions as in Fig.1.

Significant effects of saturation in the adsorption step began to appear at accumulation times longer than 60s, which was soon after the end of the linear part of the plot of peak current vs. adsorption time. Therefore this value of adsorption time was chosen.

On carrying out identical experiments with and without deoxygenation of sample solutions and electrolyte, the same results were obtained, confirming that deoxygenation is unnecessary, due to the fast square wave scan in the determination step.

Using best values of experimental parameters, sensitivities of $0.7 \mu\text{A nmol}^{-1} \text{dm}^3$ and $1.3 \mu\text{A nmol}^{-1} \text{dm}^3$ for nickel and cobalt are obtained. These are approximately ten times the values obtained using an "optimised" differential pulse procedure at wall-jet electrodes [4]. A practical detection limit of 1 nmol dm^{-3} is estimated for both elements (theoretical detection limit $5 \times 10^{-11} \text{ mol dm}^{-3}$) and the linear region in the calibration plots extends up to $10^{-7} \text{ mol dm}^{-3}$. This encompasses the range of concentrations necessary to analyse in real samples.

The stripping voltammetric procedure described has good reproducibility and represents a significant improvement for the analysis of solutions containing these metal ions in continuous flow systems, being a important step towards the goal of on-line monitoring of trace metals in real time.

CONCLUSIONS

A rapid procedure for determination of traces of nickel and cobalt ions in solution using square wave adsorptive stripping voltammetry in continuous flow at wall-jet electrodes has been developed. Additional advantages over previous protocols include the suppression of the sample and electrolyte deoxygenation step and an increased sensitivity over differential pulse adsorptive stripping voltammetry of an order of magnitude.

ACKNOWLEDGEMENTS

The authors thank PEAM/SEL/516/95 for financial support.

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