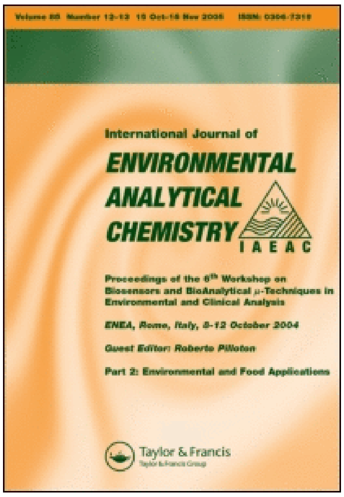

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SIMULTANEOUS DETERMINATION OF NICKEL AND COBALT BY EXTRACTION-VOLTAMMETRY IN SOIL AND LEAFY SAMPLES

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A simple, sensitive and reliable analytical method with simultaneous voltammetric determination of nickel and cobalt is described. Simultaneous voltammetric determination of Ni and Co, based on adsorptive accumulation of Ni (II) and Co (II)-xanthate (potassium propyl xanthate, PPX) after extraction into methyl isobutyl ketone on hanging mercury drop electrode (HMDE) in a single solution at a potential of -0.75 V in the 0.2 M HCl-CH_3COONa solution of pH 3.0 is reported. The reduction peaks of Ni (II)-PPX and Co (II)-PPX complexes were observed at a potential of -0.99 V and -1.125 V, respectively, by scanning the potential in the negative direction in the differential pulse mode. Extraction parameters such as pH, PPX concentration and instrumental parameters such as adsorption time, adsorption potential, scan rate etc. are optimized, and the optimized conditions are used for the determination of Ni and Co in soils and leafy vegetables. Interferences of other metal ions are studied. The lower detection limits are found to 0.35 μg/l and 0.30 μg/l for nickel and cobalt, respectively. The precision and accuracy is demonstrated by the analysis of certified reference materials (CRM's).

Keywords: Ni and Co determination; soils; leafy samples; extraction; differential pulse adsorptive stripping voltammetry

INTRODUCTION

The interest in the determination of nickel and cobalt has grown considerably in recent years owing to their involvement in some essential metabolic processes.[1,2] Nickel is a toxic trace metal[3–5] and Co an essential element.[2] Therefore, these metals need comprehensive ecochemical and ecotoxicological

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investigations on their fate and behavior in ecosystems of terrestrial and aquatic environment. Moreever, Ni is among the toxic metals a significant topic of environmental surveillance, food control and occupational medicine, toxicity and hygiene.[3] A basic prerequisite for meaningful results in the variety of application areas constitute reliable, sensitive and convenient analytical procedures suitable for routine applications. Powerful and reliable trace analytical procedures are therefore required for both metals which combine high sensitivity with satisfactory accuracy and precision. During recent years it has been established by numerous applications and extended studies that suitable modes of voltammetry provide with respect to the above stated basic trace analytical requirements one of the most superior and for a number of matrix types even the presently optimal analytical approach to determine toxic trace metal levels. Adsorptive stripping voltammetry has been considered to be one of the most sensitive methods in electroanalytical techniques for the determination of trace metal ions.[6–8] It has been shown that adsorption of metal complexes can be used as a preconcentration step to achieve the low level of detection of metal ions. Dimethyl glyoxime,[9] nioxime[10] and dioxime[11] have been used as a complexing agent for the adsorptive stripping voltammetric determination of Ni and Co. Van den Berg[12] and Zhang[13] have determined directly dissolved Ni and Co in sea water by differential pulse cathodic stripping voltammetry. Ni has been determined in natural water, and sediments[14] and human nails[15] by adsorptive stripping voltammetry. Xanthates are good chelating agents for many metal ions and preconcentration based on complexation with xanthates are known. In the present investigation, potassium propyl xanthate (PPX) has been used as a chelating agent for simultaneous determination of Ni and Co in leafy and soils in a single solution.

This paper describes the factors relevant for the differential pulse voltammetric determination of Ni (II) and Co (II) sensitized by xanthate. The application potentialities of this method are demonstrated by the analysis of soil and leafy samples.

EXPERIMENTAL

Apparatus

Differential pulse voltammetric measurements were made with a Metrohm unit coupled E506 Polarecord and E612 VA scanner. A three electrode system constituted of a hanging mercury drop electrode as a working electrode, a saturated calomel electrode as a reference electrode and a platinum wire as an auxiliary electrode. The pH measurements were carried out by Elico-LI-120 digital pH meter.

Chemicals

All the chemical used were of analytical reagent grade. Potassium propyl xanthate was synthesised[16] and purified.[17] Stock solutions of Ni and Co (1 μg/ml) were prepared from Titrisol (E.Merck). Multi element standard solutions of Ni and Co (10 to 100 μg/l) were prepared from the standards. A 3.5% solution of potassium propyl xanthate was prepared in double distilled water. Buffers of different pH of the solution were prepared by mixing 0.2 M solutions of hydrochloric acid-sodium acetate (below pH 4.0), sodium acetate-acetic acid (pH 4.0–6.0) and ammonium chloride and ammonium hydroxide (above pH 7.0). The metal ions for interference studies were prepared from the corresponding metals or oxides dissolved in either hydrochloric acid, nitric acid or water.

Extraction Procedure

An aliquot of sample solution (10–150 μg/l) containing nickel and cobalt was taken in 50 ml separating funnel. The pH of the solution was adjusted to 3 with HCl-NaOH, followed by the addition of 2ml of 3.5% reagent. The contents of the funnel were shaken well, 15 ml of MIBK was added and mixture was shaken for 3 min. Exactly 10 ml of the organic phase was transferred into an electrolytic cell. After deaeration of the solution with nitrogen for 2 min, the adsorptive stripping voltammetric determination of nickel and cobalt was performed at $25 + 1$ °C using the following settings: adsorption potential E_a: -0.75 V, adsorption time t_a: 180 sec, modulation amplitude: 25 mV, scan rate: 5 mV/s and drop size: 1.4 sec.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption voltammogram of Ni(II)-PPX and Co(II)-PPX after accumulation for 180 sec at -0.75 V in 0.2 M HCl-CH_3COONa of pH 3.0. The peaks corresponding to a potential of -0.99 V and -1.125 V are due to the reduction peaks of Ni(II)-PPX and Co(II)-PPX complex adsorbed on the HMDE. Peak currents of Ni and Co with PPX as ligand was found to be depend on pH, ligand concentration, adsorption potential and adsorption time. The dependence of peak current of Ni and Co have been studied to use the best optimum condition for trace analysis of Ni and Co in various samples.

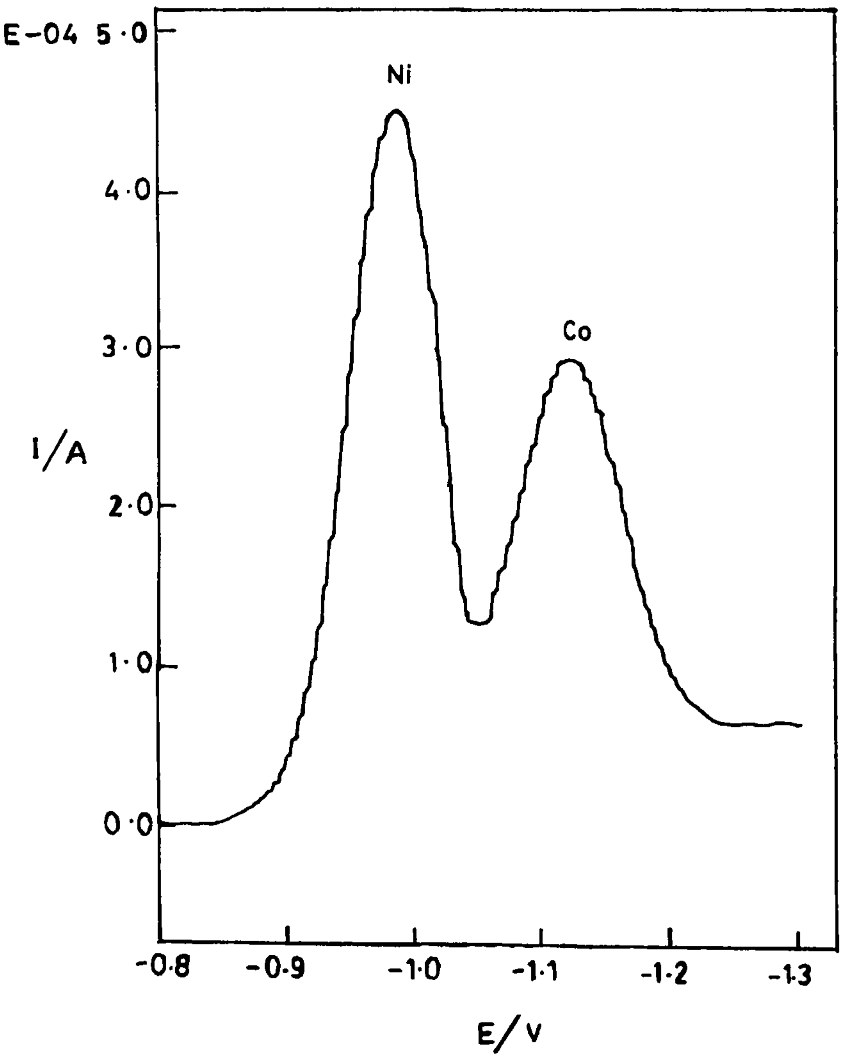

FIGURE 1 Differential pulse adsorptive stripping voltammogram of Ni (60μg/l) and Co (30μg/l) in pH 3.0 Adsorption potential: −0.75 V Adsorption time: 3 min scan rate: 5 mV/sec

Effect of pH

The pH of the solution has a marked effect on the formation and extraction of the ion associate. The experiments were conducted 60 μg/l Ni and 30 μg/l Co, 2 ml of 3.5% reagent in the pH range 2.0–12.0. The quantitative extraction was maximum at pH 3.0, hence pH 3.0 was used for the analysis.

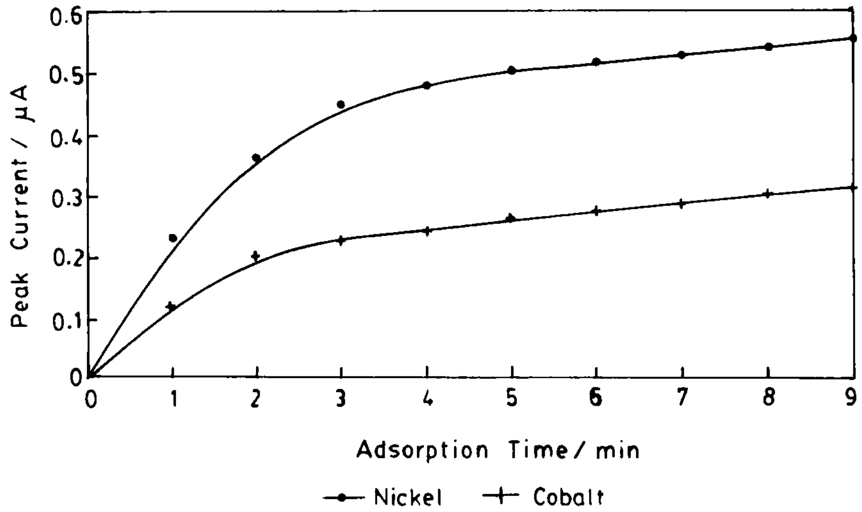

FIGURE 2 Effect of adsorption time on peak currents of Ni (60 μg/l) and Co (30 μg/l) in pH 3.0 Adsorption potential: −0.75 V Scan rate: 5 mV/sec

Effect of Ligand Concentration

Experiments were performed using the 1 to 10 % solution of PPX and 60 μg/l Ni and 30 μg/l Co, keeping all the other conditions same as those in the standard procedure, It was found that the extent of extraction was complete at concentration at about 7% of PPX. Hence, 2 ml of 3.5% reagent solution were sufficient for quantitative complexation.

Effect of Adsorption Potential

The peak height of Ni (II)-PPX and Co (II)-PPX complex at HMDE exhibit a remarkable dependence on adsorption potential. The peak height increases with the adsorption potential up to −0.75 V, reaches a maximum at this potential and then decreases out side the this potential. Hence a adsorption potential of −0.75 V was used for the determination of nickel and cobalt.

Effect of Adsorption Time

The amount accumulated at the surface of the electrode depends upon the time of adsorption of the complex at HMDE. The adsorption time was varied from 1 to 6 min. As shown in Figure 2, the peak heights of Ni and Co increase linearly with increasing adsorption time up to 6 min, beyond which the increase is more gradual. An adsorption time of 3 min was used in this study.

Effect of Scan Rate

A higher scan speed results in a decrease in resolution and peak height. At lower scan rates, the analysis time becomes prohibitively long, so that a compromise must be found. When a high resolution is required, a scan rate of 5 mV/s is used and otherwise 10 mV/s or above. Scan rate of 5 mV/s was used in the present study.

Effect of Pulse Amplitude and Drop Size

An increase in peak amplitude leads to an increase in sensitivity but also a decrease in resolution. Therefore, 25 mV is mostly used as a good compromise. The size affects the peak height but not the resolution. A longer drop size yields a higher sensitivity due to the longer area. The largest drop is unstable, therefore the medium drop size of 1.4 sec was used.

Interferences

The influence of other coexisting interferents on adsorptive stripping voltammetric determination of sample containing 60 μg/l of Ni and 30 μg/l of Co was investigated. The following foreign ions (in μg/ml) did not interfere in the determination by the above procedure: Pb^{2+} (300), Cd^{2+} (325), Zn^{2+} (300), Cu^{2+} (350), Mn^{2+} (300), Cr^{3+} (400), Tl^{2+} (300), Al^{3+} (350), Fe^{3+} (400), Mo^{6+} (400), Cr^{6+} (320), Bi^{3+} (400), Sb^{3+} (350), Se^{4+} (250), W^{6+} (250), V^{4+} (400) and In^{3+} (320).

Calibration Plot

The calibration graphs for nickel and cobalt under the chosen conditions showed good linearity in the range 0.30 to 100 μg/l of nickel and 0.25 to 85 μg/l of cobalt at a adsorption potential of -0.75 V vs SCE for 3 min with a scan rate of 5 mV/s. A detection limit of 0.35 μg/l and 0.30 μg/l was estimated.

TABLE I Analytical results for nickel and cobalt in various samples

Sample	*Found* (µg/g)*		*Added*	*% Recovery*	
	Ni	*Co*		*Ni*	*Co*
Leafy samples					
Lettuce	4.93	0.870	5	99.10	98.92
Mint	4.30	1.419	5	98.92	99.10
Radish	7.13	0.740	5	99.42	99.35
Coriander	3.62	1.120	5	99.20	98.70
Soil samples					
Soil location					
Renigunta	10.83	4.80	15	98.30	98.84
M.R. Palli	12.10	3.62	15	98.98	99.32
Kapilthertham	7.200	5.10	10	99.58	99.38
Alipiri	8.920	4.48	10	99.36	99.20
Certified Reference Materials					
Orchard Leaves	1.02 ± 0.16	0.40			
(NBS SRM 1571)	(1.03 ± 0.19)**	—			
Soil	99.4 ± 6.2	39.2 ± 1.2			
CTA-FFA-1)	(99.0 ± 5.8)	(39.8 ± 1.7)			
Soil	29.4 ± 2.1	7.8 ± 0.95			
CRM 142)	(29.2 ± 2.5)	—			

* Values are the mean of three measurements

**Certified values are in the brackets

Determination of Nickel and Cobalt in Soil, Leafy Samples and Certified Reference Materials (CRM's)

The described method was applied to soil and leafy samples collected in Tirupati, including certified reference materials. About 1 g of the finely powdered sample (leafy or soil sample) in a 100 ml beaker, was digested in 10 ml of concentrated nitric acid by heating at 50 ± 1 °C, and this was followed by evaporation almost to dryness. After cooling, the residue was dissolved in 10 ml of 2M nitric acid and diluted to volume in a 100 ml standard flask with double distilled water. Table I shows the results obtained for soil and leafy samples. The values obtained for certified reference materials agree satisfactorily with the certified values. Further the recovery of 98.30–99.58% for Ni and 98.70–99.40% for Co obtained with the proposed method for the soil and leafy sample samples indicates its accuracy and reproducibility. In general, it can be concluded that the described voltammetric method with prior chelate adsorption at the electrode represents in connection with the matrix dependent pretreatment a simple, sensitive, rapid and inexpensive analytical procedure to obtain reliable information on nickel and cobalt content in different environmental samples.

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