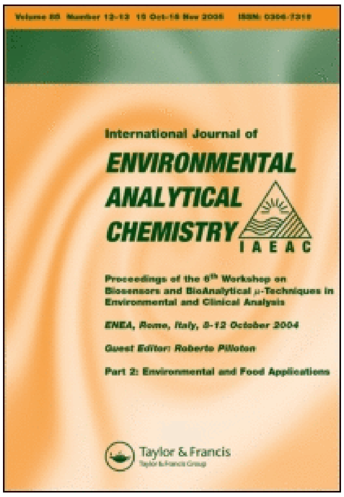

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SIMULTANEOUS TRACE DETERMINATION OF NICKEL AND COBALT IN NATURAL WATERS BY DIFFERENTIAL PULSE POLAROGRAPHY

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A differential pulse polarographic method has been developed for the simultaneous low level determination of nickel and cobalt in the presence of furildioxime in natural waters. The nature of the electrode processes was studied with cyclic voltammetry. Limits of determination of 0.4 μg/L and 0.15 μg/L were achieved for nickel and cobalt respectively

KEY WORDS: Cyclic voltammetry, cobalt, differential pulse polarography, furildioxime, nickel, trace analysis.

INTRODUCTION

The determination of trace metals at low or sub-μg/L concentrations in natural waters has led to increasing demands for sensitive and accurate analytical methods. Advanced modes of voltammetry are among the instrumental techniques for trace analysis which good have potential for speciation and quantitation studies of a number of metal ions in different matrices[1]. The main aim of the work was to develop suitable voltammetric methods for monitoring the concentration of trace metals in natural waters. The determination of lead, cadmium and iron has already been reported[2,3]. A method for the determination of nickel in industrial effluents has been developed in our laboratory[4]. This method provides a limit of detection of 50 μ/L; therefore it cannot be applied to natural water samples. In the present study a voltammetric method is described which displays better limits of detection for the simultaneous determination of nickel and cobalt.

The commonly used complexing ligands for nickel and cobalt determinations are dimethylglyoxime (dmg), thiocarbomates and furildioxime. Flora and Nieboer[5] have reported the dmg-sensitized differential pulse polarographic determination of nickel in a variety of matrices. Pihlar *et al.*[6] have reported adsorption differential pulse voltammetry for the determination of nickel and cobalt using dmg. Ammonium pyrrolidine dithiocarbamate (apdc) was used by Delves *et al.*[7] for the extraction of nickel along with cobalt from whole blood. Mikac-Devic *et al.*[8] showed the applicability of furildioxime for nickel analysis in serum and urine by atomic absorption spectroscopy. Bodrat[9] has used furildioxime in a colorimetric determination of nickel in environmental and biological materials. We have used the complexing ability of α-furildioxime to study the Ni^{2+}/Ni° and Co^{2+}/Co° systems at DME and developed suitable differential pulse polarographic conditions for the simultaneous determination of nickel and cobalt in the presence of cadmium and lead. This method has successfully been applied in the analysis of different natural water samples of Jodhpur city for their nickel and cobalt contents.

EXPERIMENTAL

Instrumentation

A PAR 174A polarographic analyzer with a drop timer (Model 174/70) and X–Y recorder (Model RE0074) was used for the dpp experiments. The instrumental settings for dpp were as follows: Modulation amplitude, 50 mV; clock time of pulse, 1 sec; scan rate, 5 mV/sec and m, 0.233 mg/sec. Potentials were measured against a saturated calomel electrode (SCE). Cyclic voltammetry was performed on a BAS CV-27 cyclic voltammograph using a hanging mercury drop electrode and Ag/AgCl as reference electrode. Cyclic voltammograms were recorded in the potential range from -0.60 to -1.20 V.

A platinum wire was used as an auxiliary electrode throughout.

Chemicals

All chemicals used were reagent grade. Standard solutions of nickel and cobalt were prepared from $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$, respectively. α-Furilidioxime used was from Sigma (Lot 1188-0570). Solutions of this ligand were prepared in ethanol (AR grade, J. Burrough).

Sampling and sample pretreatment

Different samples of drinking, tap, hand pump and lake water were collected in clean polyethylene sample containers: all glassware and sample containers were soaked in 2 M nitric acid for at least one week and washed several times with doubly distilled water. The water samples were filtered to remove the suspended particulate matter. The samples were preconcentrated 10-fold by evaporation to obtain detectable concentrations of nickel and cobalt. One liter aliquot was reduced to 100 ml which was then digested with $HNO_3 - H_2SO_4$ (10:1) to remove biological and organic matter. Subsequently, the solution was transferred to a volumetric flask and made up to volume.

All experiments were carried out in an air- conditioned laboratory at a temperature of 25 ± 1°C. The solutions were deaerated by bubbling nitrogen which was purified by bubbling through a vanadous chloride scrubbing solution for 20 min, prior to polarographic determinations.

RESULTS AND DISCUSSION

Nickel and cobalt in the presence of furildioxime in ammonia/ammonium chloride buffer (pH 9.0) showed dc polarographic waves at −0.82 and −1.03 V vs. SCE, respectively, for the reduction of Ni^{2+} and Co^{2+} to the free elements (Figure 1). To investigate the nature of the electrode processes, cyclic voltammetry was performed in which the complexes of both Ni^{2+} and Co^{2+} revealed well-defined cathodic peaks (Epc vs. Ag/AgCl: Ni; −0.86 V; Co, −1.01 V) with no corresponding anodic peak suggesting an irreversibility of the systems. A typical cyclic voltammogram of a solution containing nickel and cobalt is shown in Figure 2.

Keeping in view the irreversibility of the electrode reduction processes for both Ni^{2+} and Co^{2+}, furildioxime-sensitized dpp was carried out for their trace determination. Dpp studies revealed that the peak currents of nickel and cobalt increase with the concentration of ligand up to 1.8 mM at a fixed pH; subsequent addition of ligand did not increase the peak currents as shown in Figure 3. However, at higher concentration of furildioxime (3.0 mM), it is possible to determine nickel and cobalt

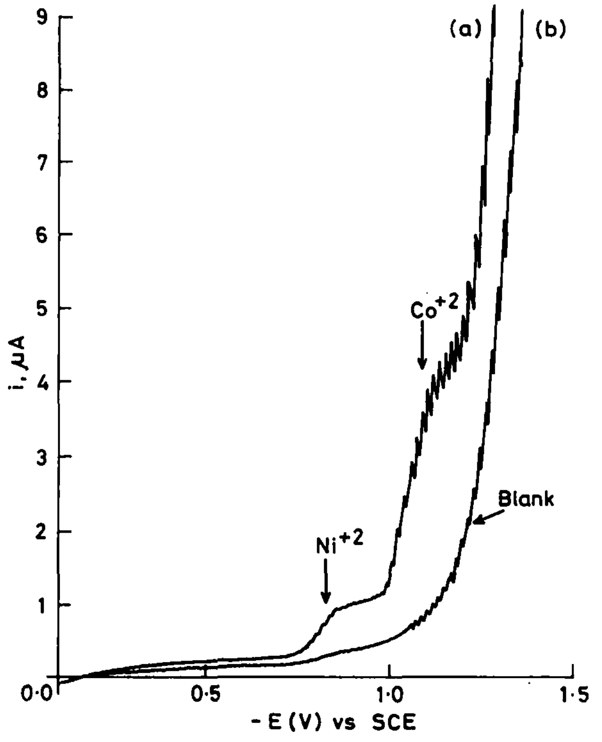

Figure 1 (a) dc polarogram of a solution of Ni^{2+} (3.41×10^{-6} M) and Co^{2+} (3.39×10^{-6} M) containing α-furildioxime (3.0×10^{-3} M) in NH_3/NH_4Cl buffer (pH 9); time constant 3 sec. (b) Blank solution containing α-furildioxime (3.0×10^{-3} M) and NH_3/NH_4Cl buffer (pH 9)

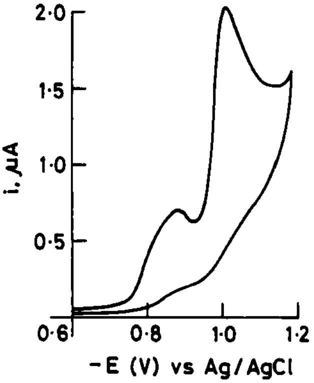

Figure 2 Cyclic voltammogram of a solution of Ni^{2+} (3.41×10^{-6} M) and Co^{2+} (3.39×10^{-6} M) containing α-furildioxime (3.0×10^{-3} M) and NH_3/NH_4Cl buffer (pH 9) at HMDE, scan rate, 60 mV/sec.

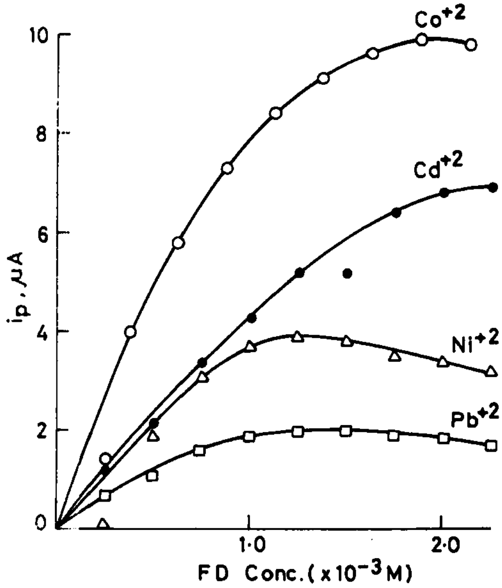

Figure 3 Dependence of peak current on ligand concentration. Pb^{2+} and Cd^{2+}, 6.0×10^{-5} M each; 3.41×10^{-6} M Ni^{2+} and 3.39×10^{-6} M Co^{2+}; NH_3/NH_4Cl buffer (pH 9).

Table 1 Peak potentials of metal ions in 3.0 mM α-furildioxime

Metal Ion	*Peak potential vs. SCE (V)*
Lead	−0.46
Cadmium	−0.74
Nickel	−0.86
Cobalt	−1.04

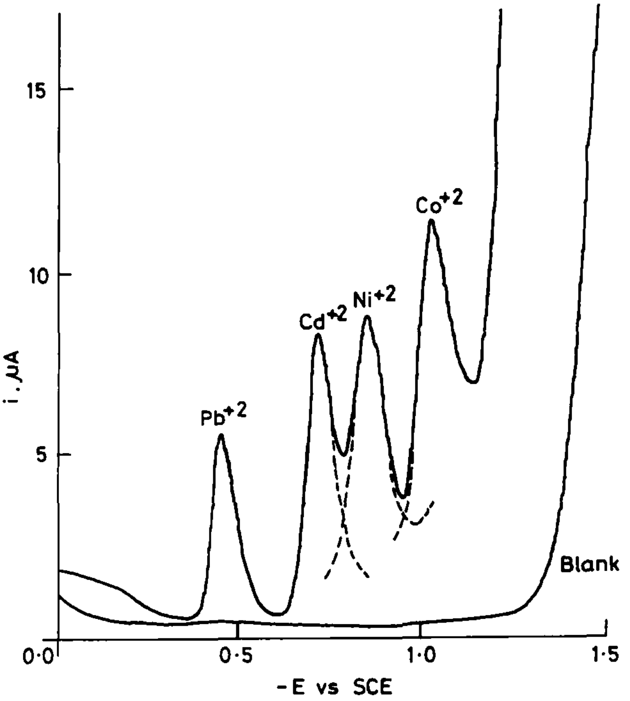

Figure 4 Dpp of a solution containing Pb^{2+}, and Cd^{2+} (6.0×10^{-5} M each), 3.41×10^{-6} M Ni^{2+} and 3.39×10^{-6} M Co^{2+}. Furildioxime, 3.0×10^{-3} M, NH_3/NH_4Cl buffer (pH 9), Modulation amplitude, 50 mV, pulse duration, 57 msec, clock time of pulse, 1 sec.

in the presence of cadmium and lead because the dp peaks for these ions were distinguishable from each other and had different peak potentials as listed in Table 1.

A dp polarogram of a solution containing Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} is shown in Figure 4. Obviously, the presence of furildioxime in ammonia/ammonium chloride buffer (pH 9.0) nickel and cobalt can be simultaneously determined without interference of lead and cadmium. Common metal ions such as copper, zinc and iron did

Table 2 Precision of Nickel and Cobalt determinations

Sample	*Nickel*			*Cobalt*		
	added (µg/L)	*found (µg/L)*	*RSD (%)*	*added (µg/L)*	*found (µg/L)*	*RSD (%)*
Synthetic	20.00	21.06[a]	7.0	20.00	21.22[a]	8.3
Natural water[c]	—	3.90[a]	13.0	—	3.07[b]	17.0

[a] $n = 5$.
[b] $n = 6$.
[c] Data of hand pump waters.

Table 3 Natural water analysis for nickel and cobalt contents by differential pulse polarography

Water sample[a]	*Nickel (μg/L)*			*Cobalt (μg/L)*		
	Min.	*Max.*	*Av.*	*Min.*	*Max.*	*Av.*
Drinking	1.06	1.76	1.35	ND[b]	ND	—
Tap	1.10	3.42	2.13	0.82	1.21	1.09
Hand pump[c]	0.94	5.80	2.70	1.40	3.52	2.27
Lake	1.12	2.40	1.49	0.80	1.50	1.16

[a] $n = 12$.
[b] ND, no detectable.
[c] Located in industrial area.

not interfere either. The relative standard deviation (rsd) was found to be 7.0% and 8.3% for nickel and cobalt, respectively (Table 2). Under these conditions well defined peaks have been observed up to a concentration of 4.0 μg/L for nickel and 1.5 μg/L for cobalt. To determine these metals at lower concentration, water samples were concentrated by 10-fold evaporation of the original sample. That is, the limits of detection were 0.40 μg/L and 0.15 μg/L for nickel and cobalt, respectively.

Determination of nickel and cobalt in natural water samples

The furildioxime-sensitized dpp reduction of Ni^{2+} and Co^{2+} was used to determine nickel and cobalt contents in drinking, tap, hand pump and lake water samples. The pretreated samples were taken to the polarographic cell with the appropriate amounts of furildioxime and supporting electrolyte to meet the conditions described above. The concentration of furildioxime was 3.0 mM and the pH of the solution was adjusted to 9.0 by adding ammonia/ammonium chloride buffer. Differential pulse polarograms were recorded in the potentials range from 0.0 to −1.3 V. The peak currents were measured at −0.86 V and −1.04 V for nickel and cobalt, respectively, after making blank corrections. The concentrations were determined by standard addition[10]. The pertinent results are summarized in Table 3.

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