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# Determination of traces of cobalt in the presence of nioxime and cetyltrimethylammonium bromide by adsorptive stripping voltammetry

Mieczyslaw Korolczuk*, Aleksandra Moroziewicz, Malgorzata Grabarczyk, Katarzyna Paluszek

*Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland*

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**Abstract**

A sensitive method of Co(II) determination by adsorptive stripping voltammetry is presented. The method exploits the enhancement of cobalt peak current observed in the system Co(II)-nioxime-cetyltrimethylammonium bromide-piperazine-*N*,*N*′-bis(2-ethanesulfonic acid). The calibration plot for an accumulation time of 60 s is linear from $5 \times 10^{-11}$ to $3 \times 10^{-9}$ mol $L^{-1}$. The relative standard deviation is 3.8% for Co(II) determination at concentration $1 \times 10^{-9}$ mol $L^{-1}$. The detection limit is $1.7 \times 10^{-11}$ mol $L^{-1}$. The validation of the method is performed by the analyses of certified reference materials and comparing the result of Co(II) determination in river water sample by the proposed method with those obtained by ET AAS. The main advantage of this new system is the micro-trace Co(II) determination by adsorptive stripping voltammetry, as compared to those described before, a low concentration of the supporting electrolyte used, and so commercially available reagents without additional purification can be used.


*Keywords:* Cobalt; Determination; Adsorptive stripping voltammetry

## 1. Introduction

In environmental and biological samples, cobalt is present at a trace level. Because it is an essential trace metal and numerous methods for its determination including spectrophotometry [1], atomic absorption spectrometry [2,3], inductively coupled plasma mass spectrometry [4] and adsorptive stripping voltammetry (AdSV) have been described. AdSV is a suitable technique for determination of traces of Co(II) because of its high sensitivity and low cost of instrumentation used. Many procedures have been proposed for Co(II) determination using HMDE [5], mercury film [6], carbon paste [7] and bismuth film electrodes [8,9]. Although, different complexing agents have been employed for the accumulation of Co(II), its dioxime complexes have gained wider use. To obtain a lower detection limit of Co(II) determination, by AdSV catalytic processes in the presence of nitrite were exploited [10–17]. The concentration of nitrite used to enhance the analytical signal is usually between 0.1 and 0.5 mol $L^{-1}$, and the Co(II) impurities in this reagent cause a high blank level. Only in paper [17] a low blank was obtained as a result of purification of nitrite by prolonged electrolysis at a mercury pool electrode.

The present paper describes a new catalytic system for Co(II) determination by AdSV. In this system, Co(II)-nioxime reduction current was enhanced by the simultaneous presence of cetyltrimethylammonium bromide (CTAB) and piperazine-*N*,*N*′-bis(2-ethanesulfonic acid) (PIPES). In this system the concentrations of contaminants in the supporting electrolyte are low and commercially available reagents without additional purification can be used.

## 2. Experimental

0.2 mol $L^{-1}$ PIPES buffers (pH = 7.4) were prepared by dissolution of piperazine-*N*,*N*′-bis(2-ethanesulfonic acid) obtained from Fluka and an adequate amount of Tracepure

* Corresponding author. Tel.: +48 81 5375592; fax: +48 81 5333348.

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$NH_4OH$ or Suprapure NaOH obtained from Merck. 0.2 mol $L^{-1}$ HEPES buffer (pH = 7.4) was prepared by dissolution of *N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid and Tracepure $NH_4OH$. 0.1 mol $L^{-1}$ nioxime (1,2-cyclohexanedione dioxime) was prepared by dissolving the reagent in 0.3 mol $L^{-1}$ NaOH (Suprapure, Merck). A standard solution of Co(II) with a concentration of 1 g $L^{-1}$ was obtained from Fluka. 0.5% solution of cetyltrimethylammonium bromide was prepared by dissolution of the reagent (Aldrich) in 0.1 mol $L^{-1}$ $H_2SO_4$. Other reagents were obtained from POCh, Poland, and used as received. Certified reference materials: estuarine water SLEW-3 and rain water TMRAIN-95 were obtained from the National Research Council, Canada. All solutions were made using triply distilled water.

### 2.1. Instrumentation

The measurements were performed using an EA 9 electrochemical analyzer and a controlled growth static mercury drop electrode in the HMDE mode, both made by MTM, Poland. The three-electrode classical cell consisted of an Hg electrode, a Pt electrode and an Ag/AgCl reference electrode was used. The Hg drop area was 2.5 $mm^2$. The solutions were de-aerated using high-purity nitrogen. UV-irradiation of water samples was carried out in quartz tubes using the UV-digester made by Mineral, Poland.

### 2.2. Sample preparation

The river water sample was filtered using a 0.45 μm membrane filter and acidified to pH close to 2 using Suprapure $HNO_3$. The river water sample and the samples of standard reference materials were digested by UV-irradiation for 3 h.

### 2.3. Standard procedure

An aliquot of the analysed sample was pipetted into the electrochemical cell and filled up to 9.3 mL with triply distilled water. Then 250 μL of $C_2H_5OH$, 100 μL of HEPES buffer and 100 μL of PIPES buffer were added. Next, 50 μL of 0.1 mol $L^{-1}$ of nioxime and 200 μL of 500 mg $L^{-1}$ CTAB were added and the solution was de-aerated for 5 min. A mercury drop was formed and the accumulation of cobalt was carried out at −0.6 V for 60 s from the stirred solution. After an equilibration time of 5 s, the differential pulse voltammogram was recorded, while the potential was scanned from −0.7 to −1.2 V at a scan rate of 50 mV $s^{-1}$. The pulse amplitude was −50 mV.

## 3. Results and discussion

The accumulation of the Co(II)-nioxime complex on the HMDE was exploited in a number of papers to determine trace concentrations of cobalt by AdSV. In papers [13,17,18] in order to enhance the analytical signal of Co(II), a catalytic process in the presence of nitrite was exploited. In this paper a new catalytic system is described. Our experiments show that the analytical signal of the accumulated Co(II)-nioxime complex can be enhanced by the simultaneous presence of the CTAB and PIPES buffer, so the optimization of the process was performed to obtain a low detection limit of cobalt determination in this new system.

### 3.1. Supporting electrolyte

Determination of Co(II) by AdSV is usually carried out in ammonium chloride–ammonium hydroxide buffer solution. In the new system described in this paper, the presence of PIPES in the buffer solution is necessary to observe the enhancement effect of the Co(II) signal, so the PIPES buffer was used as the main component of the supporting electrolyte. To enhance buffer capacity in a wider range of pH values, a HEPES buffer was added to the supporting electrolyte. To study the effect of the pH of the supporting electrolyte on the cobalt signal, a concentration of Co(II) equal to $5 \times 10^{-10}$ mol $L^{-1}$ was chosen. The change of pH was obtained by adding $H_2SO_4$ or $NH_4OH$. The obtained results are presented in Fig. 1A. For further studies pH of the electrolyte $7.0 \pm 0.1$ was chosen. It must be noted that ammonium salts, commonly used as buffer components for Co(II) determination by AdSV can be exchanged in this case for sodium salts without a decrease of the sensitivity of cobalt determination. To choose optimum concentration of the PIPES buffer its influence on the Co(II) signal was studied and the obtained results are presented in Fig. 1B. For further studies a concentration of PIPES equal to 0.002 mol $L^{-1}$ was chosen. The results obtained show that in the studied system, Co(II) determinations can be carried out at very low concentrations of the supporting electrolyte. It was an advantage of the proposed method because Co(II) present as impurity in the reagents to a lesser degree influences the blank value. The presence of $C_2H_5OH$ in the supporting electrolyte leads to better precision of the measurements.

### 3.2. Effect of nioxime concentration

Effect of nioxime concentration was studied for Co(II) at concentration of $5 \times 10^{-10}$ mol $L^{-1}$ while other standard measuring conditions remained constant. The concentration of nioxime was changed from $5 \times 10^{-6}$ to $1 \times 10^{-4}$ mol $L^{-1}$. The obtained results are presented in Fig. 1C. For further measurement, nioxime concentration of $2.5 \times 10^{-5}$ mol $L^{-1}$ was chosen. It must be noted that the measurements were carried out 5 min after the addition of nioxime to the studied solution. In the literature, usually lower concentrations of nioxime are recommended [17,18]; however, in such cases the time of Co(II) complex formation with nioxime should be prolonged. The concentration of nioxime influences a blank value so high concentrations of nioxime can not be used for

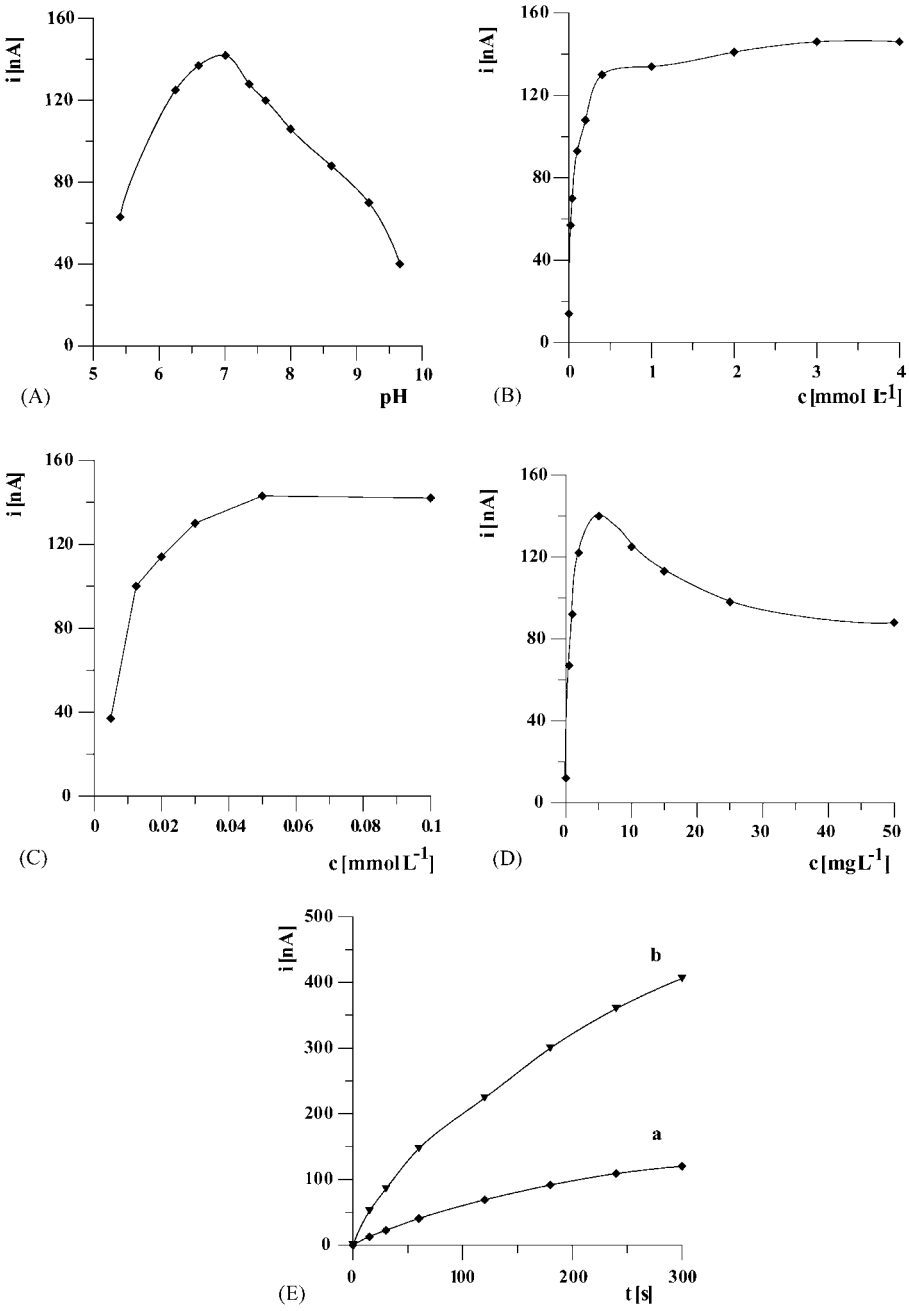


Fig. 1. The influence of: (A) pH of the supporting electrolyte; (B) PIPES concentration; (C) nioxime concentration; (D) CTAB concentration and (E) accumulation time on the cobalt peak current. For A, B, C, and D, concentration of Co(II) is $5 \times 10^{-10}$ mol $L^{-1}$. For E, concentration of Co(II) is (a) $1 \times 10^{-10}$ mol $L^{-1}$ and (b) $5 \times 10^{-10}$ mol $L^{-1}$.

the determination of Co(II) at concentrations close to the detection limit.

### 3.3. Effect of CTAB concentration

The measurements were carried out using standard conditions but CTAB concentration was changed from 0 to 50 mg $L^{-1}$. The influence of CTAB concentration on the Co(II) peak current is presented in Fig. 1D. The results show that the Co(II) peak suddenly increases as CTAB concentration increases from 0 to 2 mg $L^{-1}$ and then attains maximum at CTAB concentration of 5 mg $L^{-1}$. At higher concentrations of CTAB the peak current of Co(II) slowly decreases. The results show that to enhance the Co(II) signal in AdSV, the concentration of CTAB in the range from 2 to 50 mg $L^{-1}$ should be added to the supporting electrolyte. If not marked, a concentration of CTAB equal to 10 mg $L^{-1}$ was used in further studies.

### 3.4. Effect of accumulation time

Effect of accumulation time was studied for two Co(II) concentrations: $1 \times 10^{-10}$ and $5 \times 10^{-10}$ mol $L^{-1}$. The results obtained are presented in Fig. 1E. For both Co(II) concentrations, the peak current increases rapidly with accumulation time to 60 s. For longer accumulation times the Co(II) peak current increases slowly and the gain in sensitivity is small. Taking into account, the speed of the measurements an accumulation time of 60 s was chosen for further measurements.

### 3.5. Analytical parameters

The influence of Co(II) concentration on the peak current was studied for two concentrations of CTAB: 2 and 10 mg $L^{-1}$. For both concentrations of CTAB, the calibration plots for an accumulation time of 60 s were linear from $5 \times 10^{-11}$ to $3 \times 10^{-9}$ mol $L^{-1}$. The linear correlation coefficients were equal or higher than 0.9996. The blank value corresponds to $2.0 \times 10^{-11}$ mol $L^{-1}$. The relative S.D.s from five determinations were 3.8 and 11.2 % for Co(II) concentrations $1 \times 10^{-9}$ and $5 \times 10^{-11}$ mol $L^{-1}$, respectively. The voltammograms obtained for low Co(II) concentrations are presented in Fig. 2. The detection limit estimated from ($3\sigma$) for Co(II) concentration $5 \times 10^{-11}$ was $1.7 \times 10^{-11}$ mol $L^{-1}$. The detection limit can be further lowered by prolongation of the accumulation time and/or using lower concentrations of nioxime.

### 3.6. Interferences

The determination of Co(II) at concentration $5 \times 10^{-10}$ mol $L^{-1}$ is not influenced by $10^3$-fold amounts of Zn(II), Cu(II), Pb(II), Fe(III), As(III), Mn(II), Mo(VI) and V(V); $10^2$-fold amounts of Ni(II). In the case of higher Ni(II) concentrations, the accumulation potential should be changed to −0.79 V. As can be suspected, the presence of the surfactants causes a depression of the cobalt peak, e.g., in the presence of 2 mg $L^{-1}$ of Triton X-100, the cobalt peak decreases to 13% of its original value. The addition of EDTA to the sample solution at a concentration $5 \times 10^{-5}$ mol $L^{-1}$ causes a decay of the cobalt peak. The obtained results show that before analysis by the proposed method the sample should be mineralized. The results are in accordance with those presented in papers [18,19], where scrupulous mineralization before cobalt determination by AdSV is strongly recommended.

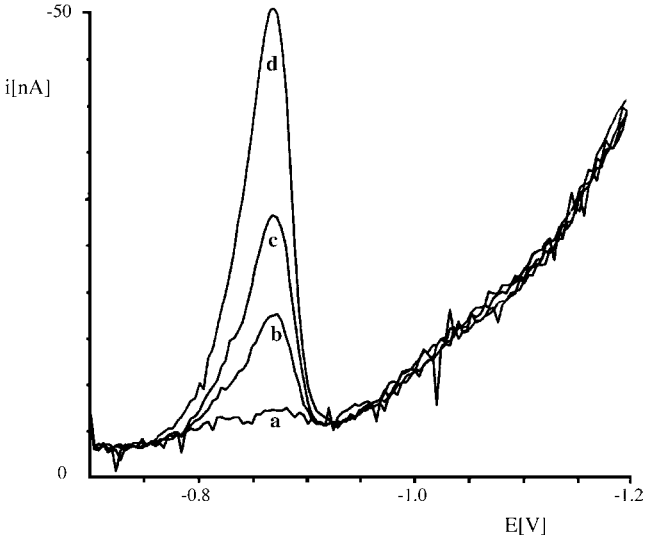


Fig. 2. The differential pulse voltammograms for different Co(II) concentrations: (a) 0 mol $L^{-1}$; (b) $5 \times 10^{-11}$ mol $L^{-1}$; (c) $1 \times 10^{-10}$ mol $L^{-1}$; (d) $2 \times 10^{-10}$ mol $L^{-1}$. Supporting electrolyte: 0.004 mol $L^{-1}$ PIPES in sodium form + 2.5% $C_2H_5OH$ + $2.5 \times 10^{-5}$ mol $L^{-1}$ nioxime + 2 mg $L^{-1}$ CTAB. Accumulation time is 60 s.

### 3.7. Analytical applications

For determination of Co(II) in real samples, the PIPES buffer in sodium form and CTAB at concentration 2 mg $L^{-1}$ were used. It was observed that the current of the cobalt peak slowly attains the final value in ca. 20 min if the sample is alkalysed before measurement to pH values distinctly differ from that corresponding to the optimal one. The above observation shows that to shorten the analysis time the sample solution should be alkalysed to the optimal pH value. It is possible that at the optimal pH value the Co(II)-nioxime complex formation is a preferential process as compared to other possible processes, e.g., the formation of other complexes with the complexing agents remaining at the trace level in the mineralised natural sample or co-precipitation of Co(II) on hydroxides of other metals present in the sample. The influence of Co(II) and Ni(II) complexation by ammonia on the analytical signal of these ions in AdSV were described in papers [19,20]. Also in paper [21] a long period of equilibration of the sample with nioxime was used before Co(II) determination in seawater sample by AdSV. A stabile signal of Co(II) in a short time in the case of analysis of real samples can also be obtained if the temperature of measurements is raised to 30 °C. The method proposed was applied to the determination of Co(II) in Bystrzyca river water and in two certified reference materials of natural water samples. The results of Co(II) determination by the proposed method are presented in Table 1. Adsorptive stripping voltammograms obtained in the course of Co(II) determination in estuarine water are presented in Fig. 3. The second peak on the voltammograms correspond to Co(II) and is well separated from preceding peak

Table 1
Results of Co(II) determination in certified reference materials and natural water sample

| Sample | Co(II) concentration (μg $L^{-1}$) | |
|---|---|---|
| | Proposed method | Reference value |
| SLEW-3 estuarine water | 0.040 (0.003) | 0.042 ± 0.010 |
| TMRAIN-95 rain water | 0.207 (0.012) | 0.22 ± 0.037 |
| Bystrzyca river water | 0.194 (0.010) | 0.180 (0.014)[a] |

In parentheses S.D.s are given ($n$ = 5).
[a] Results obtained by ET AAS.

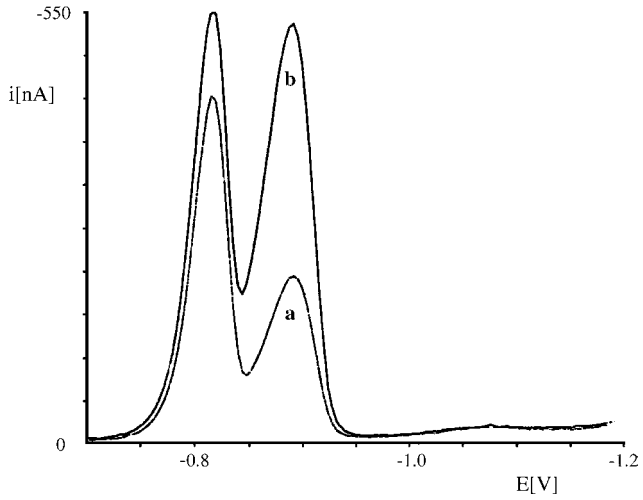


Fig. 3. The differential pulse voltammograms obtained in the course of Co(II) determination in estuarine water sample: (a) estuarine water; (b) as (a) + $1.075 \times 10^{-9}$ mol $L^{-1}$ Co(II). Accumulation time is 120 s.

of Ni(II). Table 1 also presents the certified concentrations of Co(II) for rain and estuarine water and results obtained by ET AAS for river water. In the case of Co(II) determination in river water by AAS, a multiple injection procedure was applied. Good agreement between the results obtained by the proposed procedure and those certified or obtained by AAS show that the proposed procedure can be successfully used for Co(II) determination in natural water samples.

### *3.8. Reduction process*

It is hard to give the exact mechanism of the process studied. Cyclic voltammograms (not shown) indicate that the electrode process is irreversible. The dependence, $i_p/\nu^{1/2}$ versus $\nu$, where $i_{p.}$ and $\nu$ are cobalt peak current and scan rate, respectively, decreased to a plateau value with increasing scan rate which according to [17] shows a catalytic nature of the studied process. The experiments performed in the flow system show that the enhancement effect of the Co(II) signal in the presence of CTAB and PIPES is limited only to the stripping step. The enhancement effect of CTAB on the reduction process was previously observed for In(III) and Sn(IV) [22]; however, in that case the peak increased only to the value corresponding to the reversible process. Further information on the studied system was obtained from experiments performed with $D_2O$. Exchange of 80% $H_2O$ to $D_2O$ causes a decrease of Co(II) peak to 50% of original value. The result show that $H^+$ ions take part in the overall reduction process [23]. The formation of hydrogen bubbles was not observed on the electrode even when high Co(II) concentrations were used for measurements.

## 4. Conclusion

The enhancement effect of the cobalt peak in the system Co(II)-nioxime-cetyltrimethylammonium bromide-piperazine-*N*,*N*′-bis(2-ethanesulfonic acid) can be exploited for cobalt determination by adsorptive stripping voltammetry. The advantage of this new system is a low concentration of the supporting electrolyte used and so a low blank current from reagents. The method can be applied to micro-trace cobalt determination in real samples without an additional preconcentration step. Research in our laboratory is progressing towards expanding the scope and applications of the novel catalytic system.

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