
Adsorptive stripping voltammetry of cobalt at a hanging mercury drop and mercury film electrodes: a comparative study

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Cobalt determination by adsorptive stripping voltammetry using dimethylglyoxime as a chelating agent in various buffer solutions at the hanging mercury drop (HMDE) and mercury film (MFE) electrodes are compared. Well-defined analytical peaks with very close peak potentials are obtained in the solutions of sub-microgram per liter cobalt concentrations both at HMDE and MFE. However, the residual currents using MFE are much higher than those for HMDE. The dependencies of the analytical signals on the adsorption potential have different shapes for HMDE and MFE, however, the optimal potential recommended is about -0.9 V vs. Ag / AgCl for both cases. The effect of the adsorptive accumulation time on the sensitivity of cobalt determination depends on the buffer solution composition but does not depend on the type of mercury electrode. The influence of nickel on cobalt analytical signals starts when the ratio Ni : Co exceeds 25–30 and is caused by the merging of the analytical peaks. The determination limits were evaluated as 0.05 – 0.10 $\mu\text{g l}^{-1}$ both for HMDE and MFE. The results of the comparative study indicate that from the analytical point of view the hanging mercury drop and mercury film electrode types are equivalent.

Key words: cobalt, adsorptive stripping voltammetry, hanging mercury drop electrode, mercury film electrode

INTRODUCTION

Cobalt belongs to the elements which are essential for man, animals and plants. Although usually cobalt is found in natural waters and food in trace concentrations, their variations occurring due to the natural processes or anthropogenic activities can cause deficiency or toxicity problems.

The principle of the adsorptive accumulation of nickel and cobalt chelates with dimethylglyoxime (DMG) at a hanging mercury drop electrode (HMDE) has been employed in the eighties [1, 2]. Combining the adsorptive accumulation with reductive stripping voltammetry of sorbates, the unique detection limits about 10^{-10} mol l⁻¹ (1 – 10 ng l⁻¹) have been achieved [1–6]. Although hanging mercury drop electrodes are the most suitable electrodes for adsorptive stripping techniques, they have also some disadvantages, e.g., a relatively high price and a problematic use in flow analysis systems. Very soon mercury film electrodes (MFE) were applied for cobalt determination by adsorptive stripping analysis

[7–10]. Generally, the detection limits for the flow systems using MFE were of the same range as those for HMDE. In order to achieve lower detection limits, new ligands and buffer solutions were tested, however, the detection limits for cobalt have remained between 10^{-11} and 10^{-10} mol l⁻¹ [11–13].

It should be noted that almost all the studies mentioned deal also with nickel determination, because the chelating reagents are the same and the procedures are very close both for cobalt and nickel. Moreover, the investigations are focussed mainly on nickel due to its toxicity and higher concentrations in the environment. Therefore, the abundance of studies on cobalt determination by adsorptive stripping voltammetry is only apparent and this field is still of analytical interest.

In this work, cobalt determination by adsorptive stripping voltammetry using dimethylglyoxime as a chelating agent in various buffer solutions at the hanging mercury drop and mercury film electrodes are compared.

EXPERIMENTAL

A PU-1 polarograph in a square wave voltammetry mode ($f = 25$ Hz, $V = 100$ mV s⁻¹, $E_{sw} = 90$ mV) was used for cobalt adsorptive accumulation and stripping. The same polarograph was used also as a potentiostat for depositing a mercury film. Static mercury drop stand 303 SMDE controlled by a PAR 174 A polarograph (Princeton Applied Research) was used for comparative measurements with HMDE ("small" drop size). Voltammograms were recorded on an N 307 xy-recorder or with home-built computerized equipment.

Mercury films were deposited electrochemically on a 8 mm² area glassy carbon electrode (F 3500, Radiometer) from stirred 50 mg l⁻¹ Hg²⁺ ion solution in 0.05 mol l⁻¹ HCl. The deposition potential and the time were -1.1 V and 5 min, respectively. After 10–15 measurements the mercury film was wiped off from the glassy carbon electrode with wet filter paper, and after a short polishing with a slurry of fine calcium carbonate powder a new film was deposited. All potentials were measured against a saturated Ag / AgCl reference electrode. The auxiliary electrode was platinum wire.

All chemicals were of analytical grade. Stock solution of dimethylglyoxime 0.1 mol l⁻¹ in ethanol was used. Distilled or double-distilled water was used throughout the study. Purging by nitrogen was used to remove dissolved oxygen from the solutions.

The composition of the buffer solutions used was following: 1) ammonia buffer (pH 9.4) – 0.1 mol l⁻¹ of NH₄Cl and NH₃, 2) boric buffer (pH 9.4) – 0.01 mol l⁻¹ of H₃BO₃ and NH₃, 3) triethanolamine buffer (pH 8.0) – 0.4 mol l⁻¹ NH₄Cl and 0.04 mol l⁻¹ triethanolamine (TEA).

RESULTS AND DISCUSSION

Adsorptive stripping voltammograms obtained in three most frequently used buffering media with a 1 μg l⁻¹ cobalt concentration in the identical accumulation and stripping conditions for mercury film and hanging mercury drop electrodes are presented in Fig. 1. The small peaks about 0.1 V more positive than the well-defined cobalt peaks belong to the traces of nickel in distilled water. The parameters of cobalt analytical peaks shown in voltammograms are given in Table 1.

One can see from the voltammograms that at least for the cobalt concentration range 1 μg l⁻¹ the shapes of the baselines allow a simple graphical evaluation of the peak heights in all cases. On the

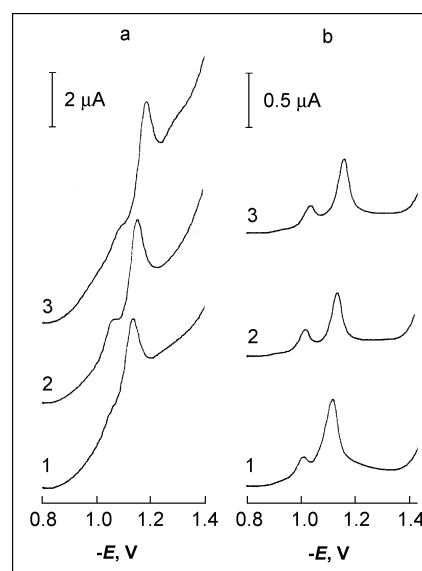


Fig. 1. Analytical adsorptive stripping voltammograms in various buffer solutions at mercury film (a) and hanging mercury drop (b) electrodes. 1 – TEA/NH₄Cl (0.04/0.4 mol l⁻¹); 2 – NH₃/NH₄Cl (0.1 mol l⁻¹); 3 – NH₃/H₃BO₃ (0.1 mol l⁻¹). Conditions: adsorption potential -0.8 V; adsorption time 60 s; 0.6 mmol l⁻¹ DMG; 1 μg l⁻¹ Co²⁺

Table 1. Parameters of cobalt analytical peaks presented in Fig. 1

Electrode	Parameter	Buffer solution		
		TEA/NH ₄ Cl	NH ₃ /NH ₄ Cl	NH ₃ /H ₃ BO ₃
HMDE	I_p^* , μA	0.70 / 0.88	0.50 / 0.63	0.58 / 0.73
	E_p , V	-1.12	-1.14	-1.16
MFE	I_p^* , μA	3.0 / 9.9	3.3 / 10.4	3.1 / 12.8
	E_p , V	-1.12	-1.16	-1.20

* Peak heights I_p values measured from baseline / from zero line

other hand, the residual currents using the mercury film electrode are much higher than those for the hanging mercury drop electrode – the ratios of the peak heights measured from the zero line and from the base line are about 3–4 for MFE and only 1.3 for HMDE (Table 1). Thus, from this point of view the MFE has a disadvantage against HMDE, because the possibility to increase the geometric peak heights significantly by choosing a higher sensitivity of the recorder is limited.

A slight shift of cobalt peak potentials to the negative side in the range of triethanolamine, ammonia and boric buffer solutions can be seen from Table 1 for both electrodes, but the peak potential differences between the electrodes are not significant. Naturally, due to the different surface areas of HMDE and MFE, the peak heights expressed in

current units are also different, however, the analytical signals of cobalt in various buffer solutions do not differ significantly.

It has been found that the analytical signals of cobalt increase with the mercury film thickness up to 0.1 μm, what corresponds approximately to 5 min of mercury plating in the conditions used. Therefore, this plating time has been chosen for all experiments with MFE.

In order to find the optimal concentration of buffer solutions, the dependencies of analytical signals on buffer concentration in the range 0.02–0.2 mol l⁻¹ have been investigated. The types of the dependencies were very close both for HMDE and MFE – the analytical signals increased up to buffer concentrations 0.05–0.1 mol l⁻¹ and then became stable (boric and triethanolamine buffers) or slightly decreased (ammonia buffer). Therefore, the optimal buffer solution concentration of 0.1 mol l⁻¹ has been chosen. It should be noted that the effect of the concentration of dimethylglyoxime on cobalt analytical signals is very similar, *i.e.* the signals do not increase much after the DMG concentration reaches 0.5–0.6 mmol l⁻¹.

An important parameter of the adsorptive accumulation influencing the sensitivity of cobalt determination is the adsorption potential. The effects of adsorption potential on cobalt analytical signals using MFE and HMDE are compared in Figs. 2 and 3. One can see that for the case of MFE there is the well-defined maximum about –0.9 V for all buffer solutions, whereas for HMDE the analytical signals do not change much in the potential range of –(0.5–0.9) V. Interestingly, from this point of view the adsorptive behaviour of cobalt and nickel chelates with DMG is different – there is no decrease of nickel analytical signals when the adsorption potential is changed from –(0.7–0.8) V to the positive

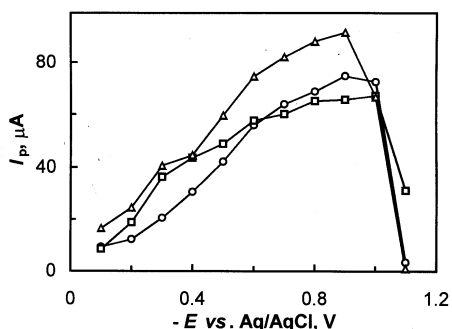


Fig. 2. Dependence of cobalt analytical signals on the adsorptive accumulation potential in various buffer solutions for MFE. Buffer solutions: Δ – TEA/NH₄Cl (0.04/0.4 mol l⁻¹), ○ – NH₃/NH₄Cl (0.1 mol l⁻¹), □ – NH₃/H₃BO₃ (0.1 mol l⁻¹). Conditions: adsorption time – 30 s; 0.25 mmol l⁻¹ DMG; 100 μg l⁻¹ Co²⁺

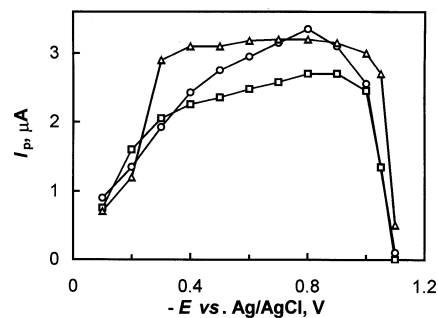


Fig. 3. Dependence of cobalt analytical signals on the adsorptive accumulation potential in various buffer solutions for HMDE. Buffer solutions: Δ – TEA/NH₄Cl (0.04/0.4 mol l⁻¹), ○ – NH₃/NH₄Cl (0.1 mol l⁻¹), □ – NH₃/H₃BO₃ (0.1 mol l⁻¹). Conditions: adsorption time – 30 s; 0.25 mmol l⁻¹ DMG; 10 μg l⁻¹ Co²⁺

side and Ni-DMG chelate is absorbed even without the external potential [14]. The possible explanation can be the well known ability of Co²⁺ to be oxidized to Co³⁺ by dissolved oxygen in the presence of strong ligands. In this case, of course, the adsorption of a charged chelate can be different. To test the effect of Co²⁺ oxidation on the analytical signals, two measurement series have been performed: a) Co²⁺ ions were added to non-deaerated buffer solution containing DMG, b) Co²⁺ ions were added to a solution of the same composition after oxygen removal. It has been found that if other conditions are identical the difference between analytical signals of both series is not significant. Therefore, the conclusion can be made that this analytical technique is not sensitive to the Co²⁺ and Co³⁺ species ratio. It should be noted that in all analytical works dealing with cobalt determination by adsorptive stripping voltammetry only Co²⁺ ions are considered, and this indirectly indicates that the effect of Co³⁺ is at least negligible.

The dependence of the analytical signals on accumulation time is one of the most important parameters influencing determination sensitivity in all techniques of stripping analysis. In the case of adsorptive accumulation these dependencies are not linear due to the electrode surface saturation by sorbate. The effect of adsorptive accumulation time on cobalt analytical signals using three buffering media at MFE and HMDE is shown in Fig. 4. For comparison of all dependencies, the analytical signals were normalized dividing them by their values in the same conditions at a 5 min accumulation time. One can see that the shapes of the dependencies are the same both for HMDE and MFE, however, they depend on the composition of the buffer solution. The deviations from the linearity increase in the range of boric, ammonia and triethanolamine buffers.

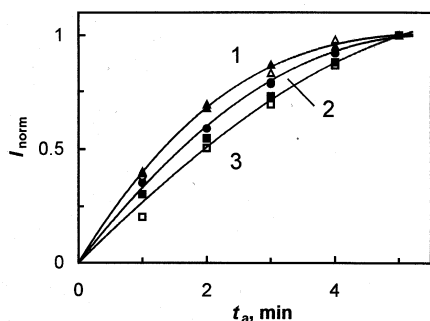


Fig. 4. Dependence of the analytical signals of cobalt on adsorptive accumulation time at mercury film and hanging mercury drop electrodes (empty and filled symbols for MFE and HMDE, respectively). The analytical signals are normalized dividing by those obtained under the same conditions at a 5 min accumulation time. 1 (Δ , \blacktriangle)– TEA/ NH_4Cl ; 2 (\circ , \bullet) – $\text{NH}_3/\text{NH}_4\text{Cl}$; 3 (\square , \blacksquare)– $\text{NH}_3/\text{H}_3\text{BO}_3$. Conditions: adsorption potential -0.8 V ; 0.25 mmol l^{-1} DMG; $0.5\text{ }\mu\text{g l}^{-1}$ Co^{2+}

Dependencies of the analytical signals on the cobalt concentration also deviate from the linearity and the reasons are the same as for the “accumulation time – analytical signals” dependencies. Naturally, in this case the deviations can be minimized by a proper choice of accumulation time – the higher cobalt concentration the lower adsorptive accumulation time should be applied. Figure 5 illustrates the dependence of analytical signals on cobalt concentration in the range $0.05\text{--}1.80\text{ }\mu\text{g l}^{-1}$. To compare the shapes of various dependencies, the analytical signals were normalized dividing them by their values at $1.6\text{ }\mu\text{g l}^{-1}$. One can see that such dependencies are the same both for MFE and HMDE, however, their shape depends on buffering solution – the linear range for the triethanolamine buffer is

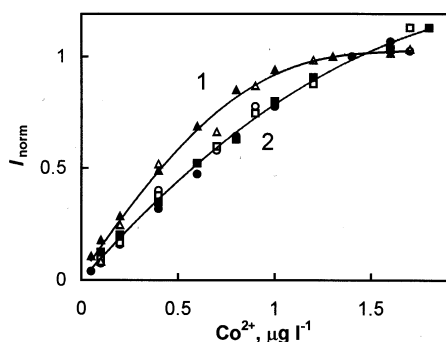


Fig. 5. Dependence of analytical signals on cobalt concentration at a mercury film and hanging mercury drop electrodes in various buffers. The analytical signals are normalized dividing by those obtained under the same conditions at $1.4\text{ }\mu\text{g l}^{-1}$ Co^{2+} . 1 – triethanolamine buffer, 2 – ammonia and boric buffers (meanings of the symbols – as in Fig. 4). Conditions: adsorption potential -0.8 V ; adsorption time 5 min; 0.25 mmol l^{-1} DMG

considerably narrower. A similar situation is observed also in the case of the higher concentrations of cobalt. It should be noted that the linearity of the dependencies is sufficient for determination of cobalt by the method of standard additions.

Since cobalt and nickel can be determined simultaneously by the same technique of adsorptive stripping voltammetry using dimethylglyoxime, their close stripping peak potentials can complicate the quantification of the analysis results. Therefore, the influence of nickel concentration on cobalt analytical signals has been investigated. It has been found that the effect of nickel on cobalt signals starts when the ratio $\text{Ni} : \text{Co}$ exceeds 25–30. A comparison of experimental voltammograms and those obtained by summation of model Gaussian peaks has shown that the interference is caused by a geometric merging of peaks. Moreover, this effect is enhanced by the shift of the analytical nickel peak potentials to the negative side with increasing nickel concentration.

Table 2 illustrates the repeatability of cobalt analytical signals at MFE and HMDE in various buffer solutions. The statistical Cochran test shows that there are no significant differences ($\alpha = 0.05$) among the variances calculated for various buffer solutions and electrodes if the cobalt concentration is the same. Therefore, the pooled relative standard deviation can be calculated as 0.04, 0.03 and 0.02 for cobalt concentrations 0.1 , 5 and $20\text{ }\mu\text{g l}^{-1}$, respectively.

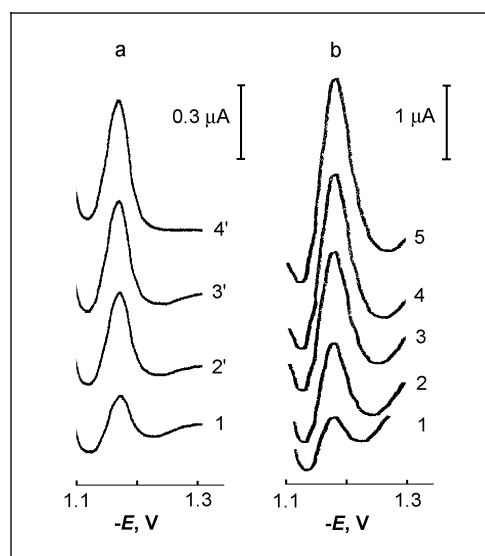


Fig. 6. Determination of cobalt in the mineral water “Tichê” by the method of standard additions at a hanging mercury drop (a) and mercury film (b) electrodes. 1 – sample of mineral water, 2’–4’ – successive additions of 0.1 , 0.05 and $0.05\text{ }\mu\text{g l}^{-1}$ Co^{2+} , respectively; 2–5 – successive additions of $0.1\text{ }\mu\text{g l}^{-1}$ Co^{2+} . Conditions: 1 ml of 1 mol l^{-1} boric buffer added to 9 ml of mineral water; adsorption potential -0.8 V ; adsorption time 5 min; 0.6 mmol l^{-1} DMG

Table 2. Repeatability of the analytical signals (relative standard deviations obtained from 10 measurements) for various concentrations of cobalt in three buffer solutions at HMDE and MFE. Conditions: buffer concentration 0.1 mol l⁻¹; 0.6 mmol DMG; E_a = -0.8 V; accumulation times for 0.1 μg l⁻¹ – 30 s, for 5 and 20 μg l⁻¹ – 5 min.

Buffer solution	Electrode	Cobalt concentration, μg l ⁻¹		
		0.1	5	20
TEA/NH ₄ Cl	HMDE	–	0.036	0.024
	MFE	–	–	0.012
NH ₃ /NH ₄ Cl	HMDE	0.043	0.036	0.026
	MFE	0.038	–	0.019
NH ₃ /H ₃ BO ₃	HMDE	0.048	0.016	0.016
	MFE	0.032	0.012	0.008

vely. It should be noted that the repeatability achieved is quite high, because the typical standard deviation for most stripping techniques is about 0.10 at the metal concentrations about 0.1 μg l⁻¹.

The evaluation of the detection limit as three standard deviations in the concentration range 0.1–0.2 μg l⁻¹ gives the values of about 10–20 ng l⁻¹ of cobalt both for HMDE and MFE at 5 min of accumulation time. However, the practical determination limit at which quantitative measurement of cobalt analytical signal can be performed is about five times higher (0.05–0.10 μg l⁻¹). Figure 6 demonstrates the analytical peaks obtained during determination of cobalt in the mineral water “Tiché” by the method of standard additions at hanging mercury drop and mercury film electrodes. The calculated results were (0.15 ± 0.04) μg l⁻¹ and (0.15 ± 0.05) μg l⁻¹ of cobalt for HMDE and MFE (at P = 0.95). Consequently, the practical analytical possibilities in the determination of trace cobalt concentrations using the hanging mercury drop and mercury film electrodes are equivalent.

CONCLUSIONS

A comparative study of cobalt determination by adsorptive stripping voltammetry using dimethylglyoxime as a chelating agent at the hanging mercury drop and mercury film electrodes has been performed. The main experimental dependencies determining the analytical characteristics are very close for both types of mercury electrodes. The detection limits obtained and the results of the determination of cobalt trace concentrations in real samples indi-

cate that from the analytical point of view the hanging mercury drop and mercury film electrodes are equivalent.

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KOBALTO NUSTATYMO ADSORBCINĖS VOLTAMPEROMETRIJOS METODU NAUDOJANT KABANČIO GYVSIDABRIO LAŠO IR GYVSIDABRIO PLĖVELINĮ ELEKTRODĄ PALYGINAMIEJI TYRIMAI

S a n t r a u k a

Atlikti palyginamieji tyrimai nustatant kobaltą adsorbicinės inversinės voltamperometrijos metodu su dimetilglioksimu, naudojant dviejų tipų gyvsidabrio elektrodus – kabančio lašo ir plėvelinį. Tyrimai atlikti trijose buferinėse terpėse – NH₃/NH₄Cl, NH₃/H₃BO₃ ir TEA/NH₄Cl. Palyginti analizinių smailių parametrai, analizinių signalų priklausomybės nuo pagrindinių nustatymo parametru (adsorbicinio kaupimo potencialo, kaupimo laiko, kobalto koncentracijos) bei analizinės charakteristikos. Kobalto nustatymo ribos įvertintos kaip 0,05–0,10 μg l⁻¹. Išmatuotos pėdsakinės kobalto koncentracijos mineraliniame vandenyje. Daroma išvada, kad abiejų elektrodų analizinės galimybės yra ekvivalentiškos.