



APPLICATION OF CATALYTIC ADSORPTIVE STRIPPING VOLTAMMETRY OF THE COBALT- α -BENZIL DIOXIME COMPLEX TO ANALYSIS OF COBALT TRACES IN METALLIC ZINC

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Summary—The catalytic adsorptive stripping voltammetric method with α -benzil dioxime and nitrite affords numerous advantages in cobalt determination. The detailed conditions of the determination of the cobalt traces in metallic zinc by catalytic adsorptive stripping voltammetry have been investigated. Both the linear sweep and the differential pulse stripping modes can be used with similar sensitivity. Possible interferences by Mn, Pb, Cu, Ni and Fe are evaluated. In the presence of 5×10^5 fold excess of Zn the linear dependence of the cobalt CASV peak current on concentration ranged from 0.05 $\mu\text{g/l}$ to 3 $\mu\text{g/l}$. Optimal conditions include the accumulation potential of -0.65 V and the accumulation time of 10 sec. The results of the determination of $10^{-3}\%$ level of Co in the metallic zinc showed good reproducibility (relative standard deviation, RSD = 0.07) and reliability.

Reliable analytical control of the Co amounts in a zinc plant electrolyte and metallic zinc is very important because the contamination of cobalt in a zinc plant electrolyte can affect the efficiency of the deposition process and the quality of the product.¹ In the analyzed zinc materials the concentration of zinc exceeds that of Co 10^5 up to 10^7 times and for this reason the determination of the Co traces in the presence of the interfering zinc matrix creates a serious problem in atomic absorption spectroscopy, spectrophotometry and voltammetry.¹⁻⁴ In most supporting electrolytes the half-wave potentials of Co and Zn are similar which causes that the voltammetric waves of both elements are badly resolved.¹

A great excess of Zn hinders the determination of Co traces by the sensitive adsorptive stripping voltammetric (ASV) method with dimethylglyoxime (DMG) because of a small difference in the peak potentials of Co and Zn in the ammonia buffer solution containing DMG.^{2,5-7} In the new approach to the problem the Zn interference is eliminated by replacing DMG by other dioximes (α -benzil dioxime, α -fural dioxime) and utilizing the catalytic effects which appear during the reduction of Co/II/-dioxime (DMG, nioxime, α -benzil dioxime, α -fural dioxime) complexes in the presence of nitrite ions.⁸⁻¹¹ As a result of the com-

binated adsorptive and catalytic effects the voltammetric signal for Co in the presence of nitrite is significantly increased. Moreover, in the ammonia buffer solutions containing nitrite and α -benzil dioxime (α BD) or α -fural dioxime (α FD) the difference in Co and Zn peak potentials ranges from 180 mV to 250 mV and is greater than in solutions containing DMG.^{10,12} Thus, due to the applied catalytic effect in a solution consisting of nitrite and α BD or α FD, the selectivity of the voltammetric stripping method of Co determination *vs* Zn is substantially enhanced. The principles of the catalytic adsorptive stripping voltammetric method (CASV) of the Co determination with α BD and α FD have been presented in the previous papers.^{10,12} Furthermore, the differential pulse CASV method with α BD and nitrite has been successfully utilized for continual on-line monitoring of cobalt concentrations in highly purified zinc plant electrolyte at Pasmico Metals EZ zinc plant in Risdon, Australia.¹³

In the present paper the results of detailed investigation of the possible interferences originating from elements usually contained in metallic zinc and in the zinc plant electrolyte, and affecting the Co determination in the presence of a great excess of zinc are reported. The application of linear scan and differential pulse

CASV method with α BD and nitrite for the analysis of Co traces in metallic zinc is also demonstrated.

EXPERIMENTAL

Apparatus and reagents

The voltammetric equipment consisted of a Pulse Polarograph PP-04 (Unitra Telpod, Kraków), a static mercury drop electrode SMDE-2 (Laboratorni Pstroje, Prague) applied in the hanging mercury drop electrode mode (a "large" drop size), a Pt wire as a auxiliary electrode and a silver-silver chloride (3M KCl) reference electrode. All potentials are reported with respect to this reference electrode. The voltammetric curves were recorded with XYT recorder Model MF-8051 (Bioanalytical System).

All solutions were deoxygenated with argon for 7 min prior to the commencement of the voltammetric determination and a flow of argon was maintained over the solution during the measurement. After each standard addition of cobalt into the voltammetric cell the solution was deaerated for 30 sec.

A stock solution of 4M ammonia buffer was prepared from Merck Suprapur grade reagents ammonia and ammonia chloride. A stock solution of $1.3 \times 10^{-3}M$ α -benzil dioxime was prepared by dissolving an appropriate amount in 96% ethanol.

NaNO_2 was recrystallized by dissolution in distilled hot water followed by addition of ethanol and cooling to 0°C.

A sample of electrolytic zinc (approx 1 g) was dissolved in 4 cm³ of 70% perchloric acid, the obtained mixture was cooled, and after dissolving in 20 cm³ of distilled water, the solution was transferred into a 50 cm³ volumetric flask and diluted with water. The final concentration of the solution was $\sim 0.3M \text{ Zn}^{2+}$.

Procedure

The following conditions were used throughout: deposition potential; -0.65 V deposition time; 30 sec (20 sec with stirring the solution, then the stirrer was stopped and deposition was continued during 10 sec quiescent period) or 10 sec without stirring. Scan rate; the potential scan was carried out in the linear sweep mode using scan rate 27 mV/sec.

Co determination in high purity zinc. A 10 cm³ of stock solution containing 0.4M ammonia buffer, $1.3 \times 10^{-5}M$ α BD and 0.5M NaNO_2 was

pipetted into the voltammetric cell and the voltammogram of blank was recorded from -0.65 V to the reduction of zinc ($\sim -1.2 \text{ V}$) after 10 sec adsorptive accumulation of Co-dioxime complex at -0.65 V without stirring. This gives the background scan. Next an appropriate volume (usually 200 μl) of the solution of the dissolved zinc was added into the blank solution and pH was adjusted to 9.0–9.6 by addition of concentrated ammonia. After 30 sec of deoxygenation the voltammogram was recorded with the same conditions as for blank. The Co content was quantified by the standard addition method.

RESULTS AND DISCUSSION

Figure 1 shows the DP ASV curves obtained for 10,000 times diluted zinc plant electrolyte in the supporting electrolyte of 0.4M ammonia buffer (b) and in the presence of $1.3 \times 10^{-5}M$ α BD (c) or simultaneous presence of $1.3 \times 10^{-5}M$ α BD and 0.5M NaNO_2 (d). As it is seen from curve (c) in the supporting electrolyte composed of 0.4M ammonia buffer, $1.3 \times 10^{-5}M$ α BD after 30 sec of accumulation at -0.65 V the peak of Ni at -0.78 V and the peak of Co at -0.98 V are observed on the voltammogram well separated from the Zn re-

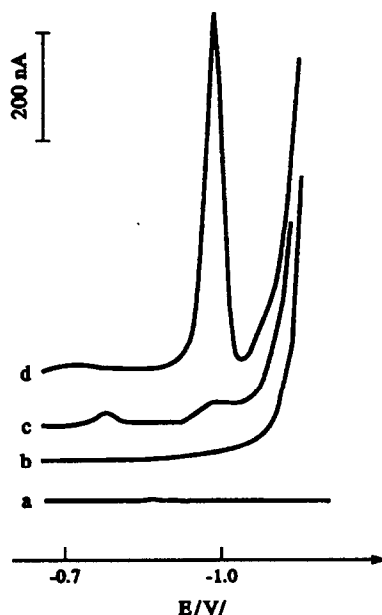


Fig. 1. Differential pulse adsorptive stripping voltammetry for: (a) 10 ml supporting electrolyte of 0.4M ammonia buffer; (b) (a) + 100 μl of aliquot of the hundred-fold diluted zinc plant electrolyte; (c) (b) + $1.3 \times 10^{-5}M$ α BD; (d) (c) + 0.5M NaNO_2 . Accumulation time $t_{\text{acc}} = 30 \text{ sec}$, $E_{\text{acc}} = -0.65 \text{ V}$.

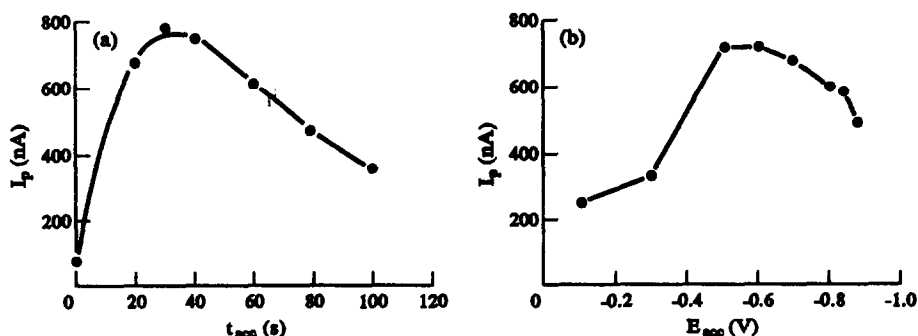


Fig. 2. The dependence of the DP catalytic ASV peak current of Co ($0.17 \mu\text{g/l}$) in the presence of 12 mg/l Zn (content of these elements contained in 10,000 times diluted of the zinc plant electrolyte in the supporting electrolyte) on accumulation time (a) and accumulation potential (b).

duction process. A addition of NaNO_2 to the solution causes 20-fold enhancement of the ASV peak current of Co and enables to determine Co traces in $10^{-9}M$ level in the presence of Zn matrix in the concentration at least $2 \times 10^{-4}M$, Fig. 1(d). For six subsequent measurements of DP CASV peaks of Co, as in Fig. 1(d), the average peak current was 660 nA, with the range of 655–670 nA, and a relative standard deviation of 0.9%.

The maximal value of Co DP CAS voltammetric response in the presence of Zn matrix was obtained for the accumulation time 30 sec and accumulation potential from -0.5 to -0.65 V (Fig. 2). The depression of the Co peak current for accumulation time higher than 30 sec is probably due to the competing adsorption of the traces of surface active substances present in the solution as contaminations, adsorption of complex ions of competing metals or/and the competing adsorption of the free αBD ligand, whose concentration in the solution markedly exceeds that of Co- αBD complex. The short accumulation time, e.g. 10 sec without stirring guarantees the excellent sensitivity of the Co determination as well as alleviates surfactant interferences.

Interferences

The metallic zinc contains, besides Co, also other elements such as Fe, Ni, Pb at the 10^{-4} – $10^{-3}\%$ levels. In case of zinc sulfate plant electrolytes the composition of the analyzed solutions is more complex. In low purity and purified electrolyte solutions the concentration of the elements may range [1, 2]: 120 – 190 g/l Zn, 1 – 4 g/l Mn, 0.2 – 10 mg/l Co, 0.2 – 2 mg/l Ni, 0.1 – 200 mg/l Cu, 0.6 – 40 mg/l Fe, as well as the traces of such elements as Pb, As, Tl, Se, Sn, Sb,

Ge, Ag whose contents usually ranges from $1 \mu\text{g/l}$ to $200 \mu\text{g/l}$.

In the CASV method of Co determination the interferences may be caused by high concentration of the accompanying elements producing a reduction current near the peak of Co, by competitive adsorption of the elements which can form complexes with αBD and adsorb on the surface of the electrode as well as by the elements which can competitively participate in the catalytic reactions. Because the CASV current of the Co in the presence of a great excess of Zn is at least by 10^3 orders of magnitude higher than that of a simple reduction process, only Zn and Mn present in zinc plant solutions in high concentrations could be included into the first group of the interfering elements. The Zn effect on the CASV response of Co was discussed in detail in the previous work.¹⁰ Mn is not reduced in a potential range from -0.65 to -1.1 V and in the investigated supporting electrolyte containing $0.4 \mu\text{g/l}$ Co and 95 mg/l Zn, it was found that the $550 \mu\text{g/l}$ Mn did not interfere with the CASV peak of Co. Addition of the $260 \mu\text{g/l}$ Pb to the solution containing $1 \mu\text{g/l}$ Co and 95 mg/l Zn did not produce any effects on the CASV peak current of Co.

Among the elements forming complexes with dioximes the effect of Cu, Fe(III) and Ni on the value of the peak current of $1 \mu\text{g/l}$ Co in the presence of 95 mg/l Zn was examined. As it has been found Cu in the concentration $130 \mu\text{g/l}$ does not affect the value of Co peak current.

The presence of Fe(III) in the concentration $110 \mu\text{g/l}$ ($c_{\text{Fe}}: c_{\text{Co}} = 110$) did not induce the occurrence of an additional catalytic peak in the vicinity of the Co peak nor any interference (Figs 3c and d). In the supporting electrolyte of $0.4M$ ammonia buffer, $1.3 \times 10^{-5}M$ αBD , $0.5M$

NaNO₂, within the Fe(III) concentration range equal to 1–5 mg/l ($c_{\text{Fe}}:c_{\text{Co}} = 1000\text{--}5000$) considerably exceeding the concentration ratio of Fe:Co in the analyzed materials, there appear on the voltammograms two peaks, presumably attributed to the two-step reduction of the Fe(III)- α BD complex with the potentials $E_p = -0.71$ V and -1.04 V, out of which the more negative one, is situated near the Co CASV peak ($\Delta E_p^{\text{Co-Fe}} = 60$ mV). Above the Fe(III) concentration 1 mg/l the more negative wave of Fe begins to overlap with the catalytic adsorptive peak of Co and can interfere in the determination of the low concentration of Co (Fig. 3b). In the presence of Ni within the concentration range 2–10 μ g/l the small ASV peak of Ni- α BD complex observed at the potential $E_p = -0.78$ V does not interfere with the Co peak (Fig. 3e). At the concentration ratios of Ni to Co considerably exceeding those in the analyzed zinc materials, when the Ni concentrations is higher than 20 μ g/l the CASV peak current of the 1 μ g/l Co is depressed (Fig. 3f). Thus, the addition of 32, 70 and 130 μ g/l Ni to the solution containing 1 μ g/l Co and 95 mg/l Zn diminishes the CASV peak current of Co by 33, 50 and 70%, respectively, but this effect could be overcome by the use of a standard additions method.

Analytical utility'

Considering the advantages connected with lower dilution of the analyte and short determination time, the procedure with 10 sec of the accumulation time without stirring can be recommended for the majority of Co determinations in the analyzed zinc materials.

Two voltammetric waveforms: the linear scan and the differential pulse were tested to develop the voltammograms after the accumulation period (Fig. 4). In both procedures with and without stirring it was found that in case of a strong catalytic effect the LS CASV was a little more sensitive than the DP CASV, and the former one can be recommended for analysis. Moreover, the linear scan yielded a better signal to the background ratio than the DP wave form.

Using the standard additions method, it was established that in a solution containing 5×10^5 fold excess of Zn, the CASV peak current of Co increased linearly with the Co concentration from 0.05 μ g/l until to at least 3 μ g/l Co (r ranges from 0.998 to 1.0) for the accumulation time 10 sec without stirring. A detection limit of 0.03 μ g/l (5.1×10^{-10} M) Co in the solution containing 5×10^5 fold excess of zinc estimated from the signal-to-noise characteristics ($S/N = 3$) of the response for 0.8 μ g/l Co (10 sec accumulation time without stirring).

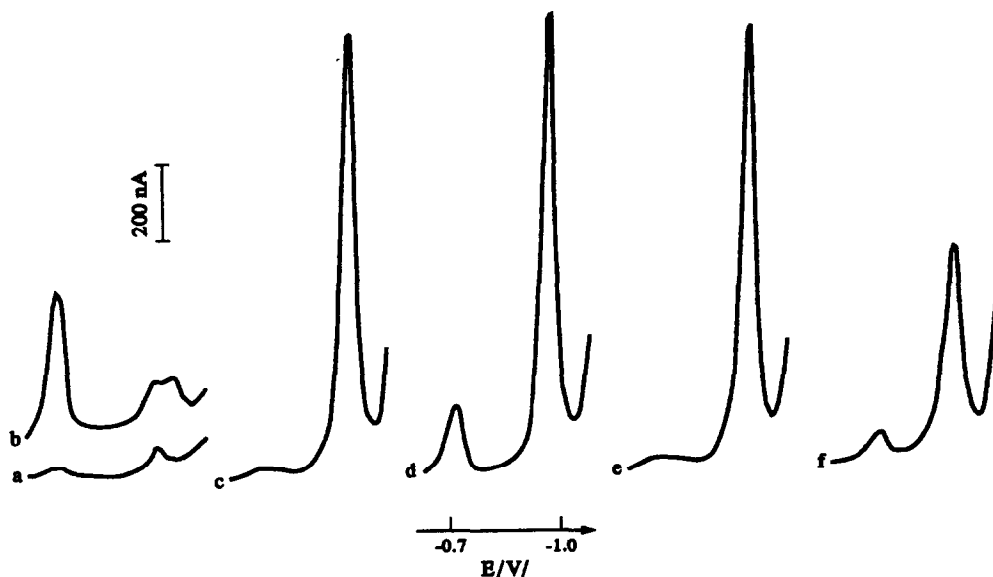


Fig. 3. The effect of iron and nickel on the DP CASV peak of Co. Supporting electrolyte: 0.4 M ammonia buffer 1.3×10^{-5} M α BD, 0.5 M NaNO₂. (a) 0.05 μ g/l Co; (b) (a) + 1.8 mg/l Fe(III); (c) 1 μ g/l Co, 95 mg/l Zn; (d) (c) + 110 μ g/l Fe(III); (e) (c) + 12 μ g/l Ni; (f) (c) + 100 μ g/l Ni. Accumulation time $t_{\text{acc}} = 10$ sec (without stirring), $E_{\text{acc}} = -0.65$ V (curves a, c–f) or $E_{\text{acc}} = -0.5$ V (curve b).

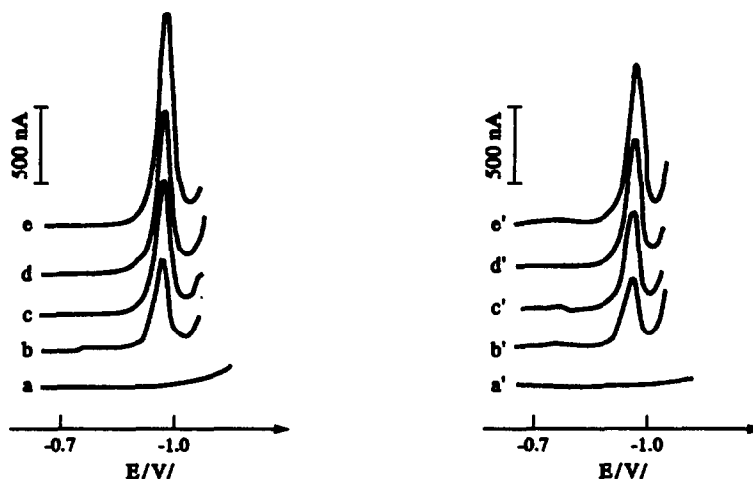


Fig. 4. Measurement of cobalt in the solution of 0.3M zinc nitrate using LS CASV (a-e) and DP CASV (a'-b'): (a, a') supporting electrolyte containing 0.4M ammonia buffer, $1.3 \times 10^{-5}M$ α BD, 0.5M NaNO₂; (b, b') a 100 μ l aliquot of 0.3M solution of zinc nitrate with addition of 40 μ g/l Co introduced to 10 ml of supporting electrolyte; (c, c') the same as (b, b') + 0.5 μ g/l Co; (d, d') the same as (b, b') + 1.0 μ g/l Co; (e, e') the same as (b, b') + 1.5 μ g/l Co. Accumulation time $t_{acc} = 10$ sec (without stirring), $E_{acc} = -0.65$ V.

To evaluate the accuracy of the method, the solution of 0.3M of Zn(NO₃)₂ was prepared from laboratory reagent of Zn(NO₃)₂ · 6H₂O, which contained approximately $5 \times 10^{-4}\%$ Fe, $5 \times 10^{-3}\%$ Pb and $1 \times 10^{-3}\%$ Ni. The content of Co in the above solution determined by the proposed CASV method using the standard addition method was equal to $(40 \pm 2.7) \mu$ g/l Co, which corresponds to $(4.53 \pm 0.31) \times 10^{-5}\%$ Co (relative standard deviation, RSD = 0.08) in solid zinc nitrate Zn(NO₃)₂ · 6H₂O. For comparison the value of $4.8 \times 10^{-5}\%$ (RSD = 0.15) was established from ICP AES determination. Next, 40 μ g/l of the Co standard solution was introduced into the solution and CASV determination of the total Co was performed (Fig. 4). The found value of the addition was equal to $(38.7 \pm 2.7) \mu$ g/l (recovery $96.8 \pm 6.8\%$).

The method was applied to determine Co in metallic zinc. For four samples of the same material dissolved in perchloric acid and analyzed twice the content of Co was found to be $6.7 \times 10^{-5}\%$ with RSD = 0.074. The method also allowed the determination of 0.1 to 5 mg/l Co in the zinc plant electrolytes with RSD ≤ 0.10 .

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