

Determination of cobalt in the presence of high concentrations of zinc by differential pulse polarography

Manfred Geißler¹ and Rui Da Maia²

¹ Research Institute for Non-ferrous Metals, Division of the VEB Mansfeld Kombinat, DDR-9200 Freiberg, German Democratic Republic

² Academy of Mining, DDR-9200 Freiberg, German Democratic Republic

Cobaltbestimmung in Gegenwart hoher Zinkkonzentrationen mit Hilfe der Differential-Puls-Polarographie

Summary. Cobalt(II) can be determined in 0.1 mol/l Na₃citrate + 0.1 mol/l NH₄Cl + 0.08% dimethylglyoxime as supporting electrolyte in the presence of a 50000-fold excess of zinc by differential pulse polarography. The limit of determination is 4.2×10^{-5} mol/l Co (2.5 mg/l). Linear calibration curves are obtained within the range of 1×10^{-7} to 5×10^{-6} mol/l cobalt without zinc and in the presence of 5×10^{-3} mol/l Zn. The analytical method developed is suitable for the determination of cobalt in zinc plant solutions.

1 Introduction

The production of zinc in various purities in electrolytic zinc solutions depends critically on the purity of the electrolyte, both for high current efficiency in the deposition stage and for product quality. Therefore, the sulfuric acid zinc electrolyte produced by leaching is purified from the contaminating elements (Ag, As, Cd, Co, Cu, Fe, Ge, Mn, Ni, Pb, Sb, Se, Te, Tl, Cl) before feeding into the electrolytic cell.

For an economic process technology the purity of the zinc electrolyte should be controlled by reliable analytical data. As the above mentioned impurity elements are removed in groups in several purification stages, it becomes possible to determine only a small number of important elements such as copper, cadmium and especially cobalt.

The typical composition of a zinc electrolyte is given in Table 1. It is obvious that the analytical problem consists in the determination of very low concentrations of copper, cadmium and cobalt in the presence of very high concentrations of zinc. Because of the high salt content ($d = 1.385$ g/ml) the zinc electrolyte has to be diluted before analyzing, but the dilution ratio is limited by the limits of determination of the analytical methods used.

Whereas it is possible to determine copper and cadmium without separation in sulfuric acid zinc sulfate solution as supporting electrolyte both by square wave polarography (SWP) [5, 6] and by differential pulse polarography (DPP) [13], the polarographic determination of cobalt is very difficult in the presence of zinc. The reduction potentials of

these two elements do not differ in the most supporting electrolytes and the resolving power of DPP is not sufficient to separate the peaks of cobalt and zinc.

Analytical techniques to determine copper and cadmium with DPP and simultaneously Cu, Cd, Pb and Sb by differential pulse anodic stripping voltammetry (DPASV) in zinc plant solutions have been described [13]. Furthermore, it has been reported [13] that the reduction and oxidation steps of cobalt are not suitable for its determination in zinc sulfate solutions using DPP. Therefore, an alternative spectrophotometric technique was proposed.

The cobalt(III)-2-nitroso-1-naphthol chelate suggested by Brainina et al. [1, 2, 8] has been used [7] for the determination of cobalt in ammoniacal supporting electrolyte (pH 9.1) using differential pulse cathodic stripping voltammetry (DPCSV). The limit of determination was in the range of 1–2 ppb and a 1000-fold amount of zinc did not interfere.

A differential pulse polarographic determination of cobalt(III)-1-nitroso-2-naphtholate after solvent extraction with benzene from citrate buffer solution has been reported [15]. In the supporting electrolyte used a 10-fold excess of zinc should not interfere.

Nangniot [11] has found that the polarographic behaviour of cobalt was improved in ammonium chloride solution in the presence of dimethylglyoxime (DMG). The electrode mechanism of the cobalt reduction in this solution has been investigated by Weinzierl and Umland [16], who have confirmed that the cobalt(DMG)₂-chelate is reduced in a two-electron-step, interfered with by high contents of zinc.

Pihlar [12] has reported that zinc does not disturb the determination of the Co(DMG)₂-complex by DPCSV.

As supporting electrolyte Chen and Neeb [3] have proposed 0.1 mol/l Na₃citrate + 0.1 mol/l NH₄Cl + DMG for the determination of cobalt in the presence of nickel and other metals using DPP. In the working range of 2–100 ppb cobalt no interferences were found for a 50- to 150-fold excess of zinc.

An adsorptive voltammetric determination of cobalt (and nickel) based on preconcentration of the DMG complex in 0.2 mol/l triethanolamine + 0.1 mol/l NH₄Cl + 0.0043 mol/l DMG has been published by Meyer and Neeb [9]. The calibration curves are linear in the ranges of 0.5 to 20 ppb Ni and 0.05 to 12 ppb Co, and a 5 to 25000-fold amount of zinc has no influence on the cobalt peak.

Due to the difficulties in the determination of cobalt in zinc plant solutions by polarographic techniques, the mostly used method is the photometric determination with 1-nitroso-2-naphthol [10, 13, 14].

Offprint requests to: M. Geißler

Table 1. Typical composition of zinc plant solutions

Element ion	[mg/l]	[mol/l]
Zn	140 ...190 ^a	2.9 ...2.14
Mn	1 ... 3.5 ^a	1.8×10^{-2} ... 6.4×10^{-2}
Cd	50 ...300	4.5×10^{-4} ... 2.7×10^{-3}
Co	1 ... 20	1.7×10^{-5} ... 3.4×10^{-4}
Cu	25 ...200	4.0×10^{-4} ... 3.2×10^{-3}
Fe	3 ... 40	5.4×10^{-5} ... 7.2×10^{-4}
Ge	0.2 ... 2	2.8×10^{-6} ... 2.8×10^{-5}
Sb	0.08... 2	6.4×10^{-7} ... 1.6×10^{-5}
F ⁻	5 ... 30	2.7×10^{-4} ... 1.6×10^{-3}
Cl ⁻	100 ...300	2.8×10^{-3} ... 8.5×10^{-3}
SO ₄ ²⁻	140 ...190 ^a	1.46 ...1.98

^a Data in [g/l]

The pH-value of the zinc plant solutions is 2–5

The object of this paper is to show a new approach to the supporting electrolyte proposed by Chen and Neeb [3] for the separation of cobalt and zinc and to the determination of cobalt in the presence of high zinc concentrations in zinc plant solutions using differential pulse polarography [4].

2 Experimental

2.1 Apparatus

Polarograms were recorded with a Radelkis Polarograph, model OH-107.

The dropping mercury electrode was self-made. As reference electrode an SCE was used produced by the Research Institut "K. Schwabe", Meinsberg (GDR). A mercury pool electrode served as counter electrode.

All polarograms were obtained at a pulse amplitude of 50 mV, a scan rate of 2 mV/s and a chart drive speed of 12 mm/min.

2.2 Reagents

All reagents were of analytical grade and dissolved in bidistilled water.

A stock solution was prepared by dissolving 0.2 mol/l sodium citrate and 0.2 mol/l ammonium chloride. For the reagent solution 1 g of dimethylglyoxime was dissolved in 100 ml methanol. The supporting electrolyte was prepared by mixing 50 ml of stock solution and 8 ml of reagent solution in a 100 ml measuring flask and diluting with bidistilled water to the mark, i.e., the final concentration of the supporting electrolyte was 0.1 mol/l Na₃citrate + 0.1 mol/l NH₄Cl + 2.77×10^{-3} mol/l DMG (pH 7.8).

2.3 Procedure

Pipette 50 ml of stock solution, 8 ml of the reagent solution and 1 ml of the sample into a 100 ml measuring flask, mix these solutions by shaking and fill up with bidistilled water to the mark. Deaerate a part of this measuring solution in the polarographic cell by passing a stream of nitrogen through it for 5 min. Record the differential pulse polarogram with the data mentioned in chapter 2.1 from -0.75 V (vs. SCE) to the reduction of zinc. Calculate the cobalt content by the standard addition method. In this case, add cobalt standard

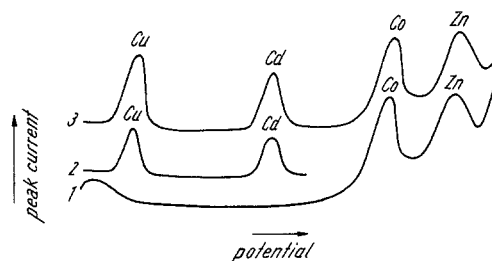


Fig. 1. Differential pulse polarograms of Cu, Cd, Co and Zn in 0.1 mol/l Na₃citrate + 0.1 mol/l NH₄Cl + 0.08% DMG. 1 5×10^{-7} mol/l Cu, Cd, Co and Zn; 2 3.15×10^{-5} mol/l Cu, 3.55×10^{-5} mol/l Cd; 3 5×10^{-5} mol/l Cu and Cd, 5×10^{-7} mol/l Co and Zn. Start potential 0.0 V

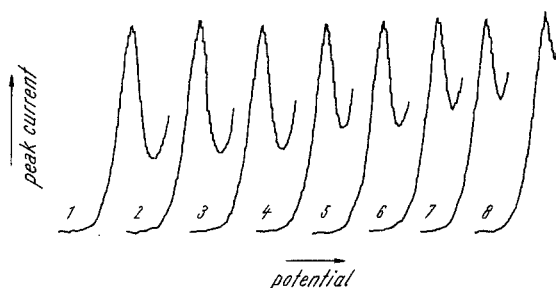


Fig. 2. Differential pulse polarograms of cobalt for different Co/Zn-ratios. Co:Zn = 1 × x; supporting electrolyte as Fig. 1. 1 x = 200; 2 x = 1000; 3 x = 2000; 4 x = 4000; 5 x = 5000; 6 x = 8000; 7 x = 10000; 8 x = 20000. Start potential -0.8 V, sensitivity 2 μA = 100 mm

solution to two separate zinc plant samples and analyze by the same procedure.

3 Results and discussion

Differential pulse polarograms of cobalt and zinc in the supporting electrolyte mentioned above are shown in Fig. 1 (polarogram 1). The cobalt peak is very well separated from the zinc peak. Characteristic for the cobalt peak is its asymmetrical shape. The more negative flank of the cobalt peak does not return to the base line. Both peaks differ in sensitivity. The peak of cobalt is much more sensitive with increasing concentration than the zinc peak. The peak potential is $E_p = -1.02$ V (vs. SCE) for cobalt and $E_p = -1.26$ V (vs. SCE) for zinc. The potential difference amounts to 240 mV.

The shape of the cobalt peak is unchanged up to a cobalt-zinc-ratio of about 1:2000 (Fig. 2). With more increasing concentration of zinc the minimum of the diffusion current between the cobalt- and zinc reduction increases continuously so that the peak of cobalt becomes more and more asymmetrical. Despite this change in the shape of the cobalt peak this peak is separated up to a concentration ratio of Co:Zn = 1:50000 and only for a ratio 1:100000 the cobalt peak is shaped as a step (see Fig. 3).

As shown in Fig. 1 (polarogram 2) copper and cadmium give separated peaks in the supporting electrolyte used. The peak potentials are $E_p = -0.24$ V (vs. SCE) for copper and

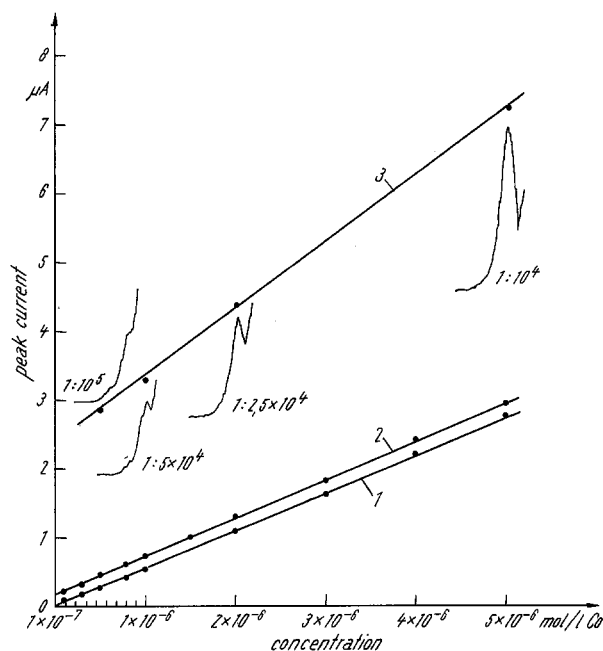


Fig. 3. Calibration curves. 1 in the absence of zinc; 2 in the presence of 5×10^{-3} mol/l Zn; 3 in the presence of 5×10^{-2} mol/l Zn. (The polarograms recorded and the Co/Zn-ratios are indicated)

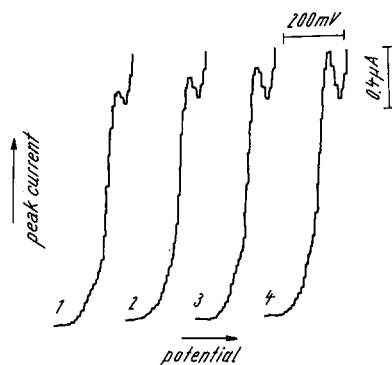


Fig. 4. Differential pulse polarograms of cobalt recorded by the standard addition method. 1 Original zinc plant solution; 2 Co-addition 1×10^{-7} mol/l; 3 Co-addition 2×10^{-7} mol/l; 4 Co-addition 3×10^{-7} mol/l. Start potential -0.75 V

$E_p = -0.65$ V (vs. SCE) for cadmium. The sensitivity of the peaks for these two elements is also much lower than that for cobalt.

Despite the fact that the peaks of the elements mentioned have different sensitivities it is possible to polarograph simultaneously Cu, Cd, Co and Zn (see Fig. 1, polarogram 3).

The calibration curve for cobalt is linear in the absence of zinc in the working range of 1×10^{-7} to 5×10^{-6} mol/l (Fig. 3, curve 1). In the presence of a constant zinc concentration of 5×10^{-3} mol/l the calibration curve is shifted in parallel (Fig. 3, curve 2), although the concentration ratio of cobalt to zinc varied from 1:50000 to 1:1000. When the zinc concentration is 5×10^{-2} mol/l the slope of the calibration curve is changed (Fig. 3, curve 3). In the latter case the cobalt-zinc ratio varied from 1:10000 to 1:100000.

As shown in Fig. 3 the d.p. polarographic curve may be recorded only up to the ratio of 1:50000.

The method developed was applied to the d.p.p. determination of the cobalt content in zinc plant solutions. The recorded polarogram of the zinc electrolyte sampled in front of the first purification stage is illustrated in Fig. 4. The cobalt content found was 2.55 mg/l when applying the standard addition method. This value is in good agreement compared with the value of 2 mg/l found by spectrophotometry with 1-nitroso-2-naphthol.

The reproducibility of the cobalt peak expressed by the mean value and the confidence interval is $\bar{x} \pm \Delta\bar{x} = (6.00 \pm 0.05) \times 10^{-7}$ mol/l ($n = 21$, $P = 95\%$) in a synthetic solution with 2.75×10^{-2} mol/l Zn and 6×10^{-7} mol/l Co. In another electrolyte the cobalt content was $\bar{x} \pm \Delta\bar{x} = 11.45 \pm 0.32$ mg/l ($P = 95\%$, $n = 11$).

Cobalt contents less than 2 mg/l as present in the feed electrolyte cannot be determined in the supporting electrolyte used.

Voltammograms recorded by cyclic triangular-wave voltammetry did not show an anodic peak. Thus it is verified that the reduction of the cobalt-dimethylglyoxime chelate is totally irreversible.

As listed in Table 1 the plant electrolyte contained a lot of further ions except copper and cadmium, which do not interfere the determination of cobalt with the method described. Manganese is not reduced in the supporting electrolyte with DMG as tested with a concentration of 6.4×10^{-4} mol/l Mn.

Although copper and cadmium give well defined peaks the peak height does not depend linearly on the concentration.

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