



Selective determination of trace cobalt in zinc electrolytes by second-derivative catalytic polarography

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Abstract: We report herein a highly selective method for directly determining the trace Co^{2+} in highly concentrated zinc electrolyte. This novel method is based on a second derivative wave of catalytic adsorptive polarography generated by complexing Co^{2+} with dimethylglyoxime and nitrite onto a dropping mercury electrode. By employing a medium with $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer, DMG and NaNO_2 during determining the trace Co^{2+} , any interferences of highly concentrated Zn^{2+} and other coexisting metal ions in the electrolyte are completely eliminated due to the selective masking effect of EDTA. When the concentration of Co^{2+} is within 1.0×10^{-10} – 3.2×10^{-7} mol/L range, it shows a good linear relationship with the current peak. Detection limit is 1.0×10^{-11} mol/L, and $\text{RSD} \leq 2.7\%$ for six successive assays. We have compared the efficiency of the current method to that obtained by cobalt nitroso-R-salt spectrophotometry, and the absolute values of relative deviations are $\leq 4.2\%$. The method developed and described herein has been successfully employed in determining the trace Co^{2+} in actual zinc electrolyte.

Key words: catalytic adsorptive voltammetry; highly selective masking; Co^{2+} determination; zinc electrolyte

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1 Introduction

Co^{2+} in a zinc electrolyte is an impurity which must be strictly controlled during the hydrometallurgical process. This impurity decreases the efficiency of produce, even leading to “plate-burning” during the deposition step [1]. Consequently, in order to induce a minimal effect, Co^{2+} maximum allowed concentration in the zinc electrolyte is 0.3 mg/L [2]. The Co^{2+} removal methods involved in various hydrometallurgical plants are based on zinc powder replacement and chemical precipitation generated by adjusting the

dosage of added reagent according to the impurity content. Therefore, a real-time and accurate determination of Co^{2+} content in the zinc electrolyte at the inlet and outlet of the cobalt removal section is required, which can provide the effective feedback information [3].

The analytic strategies which have been developed so far and are widely used for determining the Co^{2+} in zinc-containing solutions are spectrophotometry using chromogenic agents such as nitroso-R-salt [4], alpha-BD [5] and PAN [6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7], kinetic-catalytic spectrophotometry [8], atomic absorption

spectrophotometry (AAS) [9], electro-thermal atomic absorption spectrometry [10], fast sweep voltammetry [11, 12], catalytic polarography [13], adsorptive stripping voltammetry [14], catalytic adsorptive stripping voltammetry [10, 15–23], differential pulse polarography [24–27], differential pulse stripping voltammetry [28], differential pulse adsorptive stripping voltammetry [2] etc. The sensitivity and selectivity for spectrophotometry are less ideal [10] and the sample pre-treatment process is cumbersome, particularly multiple boiling [4]. In the case of ICP-AES, the matrix effect seriously influences the accuracy of determination, particularly at lower concentrations of the impurity. The instruments of ICP-AES and AAS are also expensive and require an adequate working environment, impeding their online detection application in the production field. The voltammetric methods are generally recognized as valuable tools in determining the metal ions within a complex matrix due to their high sensitivity, good selectivity and simple operation processes. Among them, polarography involves a mercury drop-based working electrode which can be constantly updated, being independent of its past history [15]. This property makes the polarography standing out as other techniques do not possess it, being also appropriate for the use in online analysis.

Most of the polarographic methods previously reported for determination of Co^{2+} content from concentrated Zn^{2+} solutions involve DMG as the ligand. Some among the approaches display an excellent sensitivity toward Co^{2+} determination, even with a detection limit of up to 10^{-11} mol/L [26]. However, Zn^{2+} in the solution also produces a polarographic wave, and the peak potentials of Zn^{2+} and Co^{2+} are very close [12]. Therefore, these methods are usually used only for determining Co^{2+} in the solution where minor Zn^{2+} interference occurs [12, 19]. If Zn^{2+} concentration $> 10^6$ times of Co^{2+} concentration, the Co^{2+} derivative wave is overlapped with the Zn^{2+} wave [3]. The issue alters the accurate determination of Co^{2+} in the zinc electrolyte. In order to mitigate the interference of Zn^{2+} and increase the efficiency of Co^{2+} determination, a plethora of distinct approaches were developed.

For example, GEIBLER et al [24] have used sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) to minimize the Zn^{2+} effect. They have involved a solution mixture

containing 0.1 mol/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 0.1 mol/L NH_4Cl and 0.08% DMG that has facilitated the determination of Co^{2+} in the electrolyte by differential pulse polarography. When the Co^{2+} - Zn^{2+} mixture has reached a 1:2000 ratio, the Co^{2+} wave has asymmetrically changed under the influence of Zn^{2+} wave; however, the detection of Co^{2+} has been impossible at ratios up to 1:50000. Subsequently, they have tailored the method by adding 1-(benzylsulfonyl)-2-(*N*-morpholino) ethane (BME) as surfactant to the original supporting electrolyte [25]. This approach has allowed the determination of 0.7 mg/L Co^{2+} in the solution containing Zn^{2+} below 160 g/L. Obviously, the method is not sensitive enough because the Co^{2+} concentration in the zinc electrolyte is usually below 0.2 mg/L. In order to improve the sensitivity of Co^{2+} determination, BOROVKOV et al [16] have modified this procedure using a supporting electrolyte with the following composition: 2 mol/L NH_4Cl + 2 mol/L NH_4OH + 2×10^{-3} mol/L DMG+ 0.2 mol/L $\text{NH}_2\text{OH} \cdot \text{HCl}$, but the modified approach can only be used to determine the Co^{2+} in the solutions containing Zn^{2+} below 140 g/L. However, the Zn^{2+} concentration in the electrolyte is usually higher than 170 g/L during the modern hydrometallurgical process of zinc, therefore, the selectivity is not suitable for determining accurately the Co^{2+} . BOBROWSKI et al [17] could easily determine the cobalt whose concentration was down to 1×10^{-10} mol/L, based on the formation of cobalt- α -benzildioxime complex; the catalysis of nitrite, however, Zn^{2+} mass concentration in the solution should be below 1.2×10^5 times the Co^{2+} . Obviously, the method's application is limited during determining the trace Co^{2+} . MRZLJAK et al [2] have determined cobalt at a hanging mercury drop electrode with in situ matrix exchange. This method used a bottom-drain flow-through cell to remove the interference of high concentration of zinc, and is of a detection limit of 0.25 $\mu\text{g/L}$ cobalt in zinc plant electrolyte, showing its high sensitivity to determine the Co^{2+} . Till now, it is the most selective, sensitive and accurate method of trace Co quantification, and has been implemented successfully for on-line control of Co traces in the zinc plant electrolyte. However, it is difficult to popularize this method because many laboratories do not have the relevant modern voltammetric instrumentation at their disposal.

For the above reasons, so far, the most widely used method for determining Co^{2+} within zinc electrolyte is still the electrothermal atomic absorption spectrometry whose reproducibility is very poor and the nitroso-red-salt spectrophotography whose operation is very cumbersome, especially multiple boiling [4]. Furthermore, both the two methods are unable to be applied in the real-time or online determination of Co^{2+} within the zinc electrolyte. Therefore, despite the multitude of above mentioned methods for determining Co^{2+} , the direct determination of the concentration of trace Co^{2+} within zinc electrolytes that can fit the industrial on-site requirements is still worth studying. We report herein the development of a new method with high selectivity and accuracy, which facilitates the trace Co^{2+} determination within zinc electrolyte by using a second-derivative catalytic polarography based on a mixture containing DMG, EDTA and NO_2^- . EDTA has the key role to annihilate the influences of Zn^{2+} and other coexisting ions; whereas DMG and NO_2^- enhance the sensitive of Co^{2+} determination. The advantages of our developed strategy also include readily available and less expensive reagents. The factors are of paramount importance for industrial online monitoring processes, providing that a wide range of samples require Co^{2+} determination. Therefore, our work is important to the improvement of Co^{2+} determination in industrial online detection.

2 Experimental

2.1 Apparatus and materials

The polarography (JP-303; Chengdu Instrument Factory, Chengdu, China) employed was equipped with a three-electrode system consisting of a dropping mercury-based working electrode, a saturated calomel electrode as a reference, and an auxiliary platinum electrode. A pH meter (pHS-3C; Shanghai Leiz Chong Yi Instrument Co. Ltd., Shanghai, China) was used for pH measurements.

The principal agents employed were $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (3.0 mol/L, $\text{pH}=8.3$), DMG ethanol solution (11 g/L) prepared by dissolving DMG (1.1 g) in absolute ethanol (100 mL), EDTA solution (1.0 mol/L) in $\text{NaOH}_{(\text{aq})}$, NaNO_2 solution (4.0 mol/L) freshly prepared prior to use, Zn^{2+}

(2.60 mol/L) and Co^{2+} (0.0100 mol/L) standard solutions were prepared by dissolving the corresponding SO_4^{2-} salts in an appropriate amount of water, further diluted to the required concentration prior to use. Both Co^{2+} and Zn^{2+} salts were guarantee reagents; the other being of analytical grade. The water was redistilled.

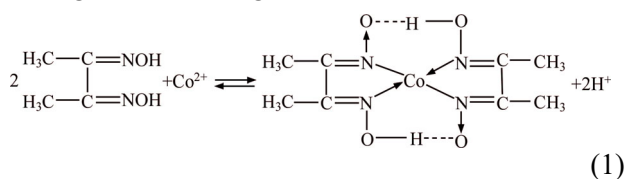
2.2 Procedure

One milliliter of zinc electrolyte (or 1.00 mL Co^{2+} and Zn^{2+} standard solutions) were transferred into a 50 mL volumetric flask, followed by adding NaNO_2 (4.0 mL) and DMG (1.4 mL) solutions, after mixing homogeneously, EDTA (3.0 mL) and $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (8.0 mL) solutions were added to the flask. The mixture was diluted to 50 mL with redistilled water, and mixed homogeneously. The solution was kept for 5 min, and subsequently transferred into an electrolytic cup, recording the second-derivative polarographic curve from -300 to -1350 mV; the peak potential corresponding to Co^{2+} was observed at about -1152 mV. The instrument parameters were: scan rate 300 mV/s, dropping mercury cycle 8.4 s, and the stationary time 6 s. All measurements were carried out at 20 ± 2 °C; all vessels were soaked with 10% HNO_3 solution, and then washed with redistilled water. The Co^{2+} concentration was calculated using the standard addition method. When the concentration of Co^{2+} in real zinc electrolyte was too high, the sample might be transferred after its quantitative dilution with dilute H_2SO_4 solution.

3 Results and discussion

3.1 Formation mechanism of catalytic adsorptive voltammetric waves of Co(II) complexes

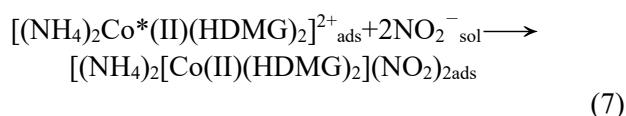
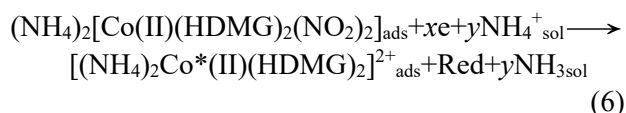
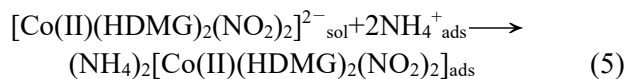
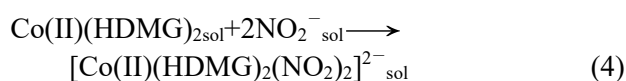
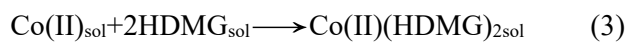
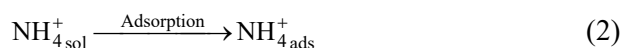
As widely known, Co^{2+} and dimethylglyoxime form a complex with a 1:2 coordination ratio, through the following reaction:



Equation (1) shows that a dimethylglyoxime molecule contains two active protons. Therefore, in order to facilitate writing, the neutral molecules may be written as “ H_2DMG ” instead of the usual “DMG”, and the anion containing an active proton

may be written as “HDMG”. It is obvious that Co^{2+} is coordinated with HDMG in solution to get Co(II)(HDMG)_2 . According to the ligand field theory, Co^{2+} adopts a d^7 electron configuration, and its ligand field is octahedral. When NO_2^- is present in the solution, the Co(II)(HDMG)_2 complex reacts further with NO_2^- , forming a mixed ligand complex $[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]^{2-}$, which also adopts an octahedral configuration.

Catalytic adsorptive voltammetric waves of the Co^{2+} complexes were studied by BOBROWSKI et al [1, 14, 17–19, 27, 29] and SUN et al [30], and it was found that the formation mechanisms vary with different reaction systems. Therefore, some related reaction systems were classified by BOBROWSKI et al [29], and the formation mechanisms of catalytic voltammetric waves in various reaction systems were also explained. According to the literatures [27, 29, 30], it is indicated that the catalytic adsorptive voltammetric wave of the Co(II) complex can form under $\text{NH}_3\text{-NH}_4^+$ buffer condition. NH_4^+ has a strong adsorption on the mercury electrode, whereas the adsorption of $[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]^{2-}$ itself on the mercury electrode is less intense. When NH_4^+ is adsorbed to the electrode surface, $[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]^{2-}$ can also electrostatically interact onto the electrode and forms $(\text{NH}_4)_2[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]$ which has a strong electrochemical activity. Under the condition of NH_4^+ , as the negative sweep voltage changes to a certain value, the complex adsorbed onto the electrode, $(\text{NH}_4)_2[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]_{\text{ads}}$ is converted to $[(\text{NH}_4)_2\text{Co}^*(\text{II})(\text{HDMG})_2]_{\text{ads}}^{2+}$, namely an adsorbed complex cation, and the NO_2^- in $(\text{NH}_4)_2[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]_{\text{ads}}$ is reduced to NH_2OH or NH_3 . $[(\text{NH}_4)_2\text{Co}^*(\text{II})(\text{HDMG})_2]_{\text{ads}}^{2+}$ can strongly adsorb the NO_2^- in the solution, reproducing $(\text{NH}_4)_2[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]_{\text{ads}}$, namely the reactant of the electrode reaction. This triggers a strong catalytic cycle current which is proportional with the Co^{2+} concentration in the solution, leading to a large increase of the peak current of Co^{2+} polarographic wave. When the reduction product, NH_2OH or NH_3 is shown with “Red”, this process to form the catalytic adsorptive voltammetric wave of the cobalt complex may be expressed as follows (subscripts “sol” and “ads” represent dissolved and adsorbed states, respectively).



The product $[(\text{NH}_4)_2\text{Co}^*(\text{II})(\text{HDMG})_2]_{\text{ads}}^{2+}$ of Reaction (6) is the reactant of Reaction (7), and the product $(\text{NH}_4)_2[\text{Co(II)(HDMG)}_2(\text{NO}_2)_2]_{\text{ads}}$ of Reaction (7) is also the reactant of Reaction (6). The two reactions can promote each other and proceed in a circular manner, consequently, a parallel catalytic process forms. Obviously, the real catalytic cycle process consists of only Reactions (6) and (7). Both the reactants and products of the catalytic cycle are in adsorbed states, and the whole reaction mechanism is also based on the adsorption onto the electrode. Therefore, the polarographic wave of the Co^{2+} is a catalytic adsorptive polarographic wave. The intermediate in the cycle process shown by Eqs. (6) and (7)), namely $(\text{NH}_4)_2[\text{Co}^*(\text{HDMG})_2]_{\text{ads}}$ plays an important catalytic role in the reduction of NO_2^- because it is not actually consumed. The consumed substances are NH_4^+ and NO_2^- which exist largely in the solution, leading to a very strong catalytic current.

3.2 Selection of masking agent

Some polyaminopoly carboxylic acids such as ethylene diaminetetraacetic acid (EDTA), ethylene glycol-bis-(2-aminoethylether)-tetraacetic acid (EGTA), ethylene diaminetetrapropionic acid (EDTP), cyclohexane diaminetetraacetic acid (CDTA) and N-(2-hydroxyethyl) ethylenediamine -N,N',N'-triacetic acid (HEDTA) can be used to mask most metal ions in the $\text{NH}_3\text{-NH}_4\text{Cl}$ solution containing DMG and NaNO_2 , but because of its preferential reaction with DMG and NO_2^- , Co^{2+} itself in the solution is not masked by the polyaminopoly carboxylic acids. These can be used to improve the selectivity for determining the Co^{2+} . However, in all the polyaminopoly carboxylic acids,

only EDTA is low-cost and easily available.

The stability constants (K_{MY}) of EDTA complexes of common metal ions are shown in Table 1 [28]. Obviously, the stability of Co(II)–EDTA complex in the solution is smaller than the complexes of most coexisting metal ions. In addition, the reaction of Co^{2+} with DMG and NO_2^- can produce a very stable mixed-ligand complex, which can form an adsorption catalysis wave. Therefore, the coexisting metal ions in the solution may be masked by adding appropriate amount of EDTA, having no interference with the Co^{2+} determination. In several metal ions whose EDTA complex stabilities are smaller than Co(II)–EDTA complex, there are Mn^{2+} , Fe^{2+} , Al^{3+} , alkaline and alkaline earth ions. In the experimental sweep voltage range, the probabilities of electrolytic reductions of Al^{3+} , alkaline and alkaline earth ions are very small. In the $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer solution, both Mn^{2+} and Fe^{2+} do not react with DMG and NO_2^- [26, 27], and only react with NH_3 to form the NH_3 -ligand complexes. The relevant study has shown that in the sweep voltage range, neither polarographic wave of $\text{Mn}(\text{II})(\text{NH}_3)_4$ nor that of $\text{Fe}(\text{II})(\text{NH}_3)_4$ will appear [29].

Table 1 Stability constants of EDTA complexes of common metal ions

Cation	$\lg K_{MY}$	Cation	$\lg K_{MY}$	Cation	$\lg K_{MY}$
Ag^+	7.32	Al^{3+}	16.11	Hg^{2+}	21.80
Na^+	1.66	Co^{2+}	16.31	Sn^{2+}	22.10
Li^+	2.79	Zn^{2+}	16.50	Cr^{3+}	23.00
Ba^{2+}	7.76	Cd^{2+}	16.53	Sc^{3+}	23.09
Sr^{2+}	8.63	TiO^{2+}	17.30	Th^{4+}	23.20
Mg^{2+}	8.69	Pb^{2+}	18.04	Fe^{3+}	25.10
Be^{2+}	9.24	Y^{3+}	18.09	V^{3+}	25.90
Ca^{2+}	10.69	Ni^{2+}	18.67	Bi^{3+}	27.94
Mn^{2+}	14.04	Cu^{2+}	18.80	Sn^{4+}	34.51
Fe^{2+}	14.33	Ti^{3+}	21.33	Co^{3+}	36.02

In an actual zinc electrolyte, there are usually many interfering metal ions except matrix Zn^{2+} . Therefore, EDTA was selected as the masking agent during determining Co^{2+} in zinc electrolytes.

3.3 Influence of EDTA and its concentration on selectivity of method

The second derivative waves of some experimental solutions were determined according

to “procedure”, and the results are shown in Figure 1. The experimental solution consisting of $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer, DMG and NaNO_2 has exhibited no polarographic wave in the sweep voltage range (Figure 1(a)). When 1.0 mL of Zn^{2+} standard solution (7.8×10^{-3} mol/L) has been mixed with solution *a* (namely forming solution *b*), a very strong second derivative wave has appeared at about -1260 mV (Figure 1(b)), and the electrolytic current has started from -1120 mV. Obviously, the second derivative wave corresponding to Co^{2+} (Figures 1(c) and (d)) will overlap with that of Zn^{2+} . In fact, the derivative wave will broaden as Zn^{2+} concentration increases, namely the electrolytic current of the Zn^{2+} will appear at a more positive potential, causing more serious overlap between Zn^{2+} and Co^{2+} derivative waves. Therefore, the Co^{2+} in the solution can not be determined in this case (particularly, the electrolyte containing high concentrated Zn^{2+} (approximate 2.6 mol/L). However, the addition of EDTA (3.0 mL) to solution *b* (namely forming solution *c*) has led to a current-potential curve (*I*–*E* curve) similar to that shown in Figure 1(a), showing that Zn^{2+} within the solution has been completely masked. When 1.0 mL of Co^{2+} (1.0×10^{-6} mol/L) has been added to solution *c*, the sensitive second derivative wave of Co^{2+} has appeared at about -1152 mV (Figure 1(c)). This result confirms the function of EDTA to selectively mask Zn^{2+} within the test solution.

In order to verify the function of EDTA to mask other impurity metal ions coexisting within the zinc electrolyte, Zn^{2+} standard solution (1.0 mL) added to solution *c* has been substituted with actual Zn^{2+} electrolyte (1.0 mL), and the *I*–*E* curve has been determined mensurated. The result is illustrated in Figure 1(d). The graph clearly indicates that the only observed polarographic wave corresponds to the catalytic adsorptive wave of the Co(II) complex; all the other ions coexisting in the actual zinc electrolyte do not interfere with Co^{2+} determination. It is also suggested that the addition of EDTA enables the selective determination of trace Co^{2+} within the zinc electrolyte. Although miscellaneous metal ions coexisting in the electrolyte can react with EDTA, forming the corresponding 1:1 chelates, Co^{2+} among them can also react with DMG and NO_2^- , leading to a more stable chelate. The chelate is so stable that its central cation, namely Co^{2+} will not be masked by

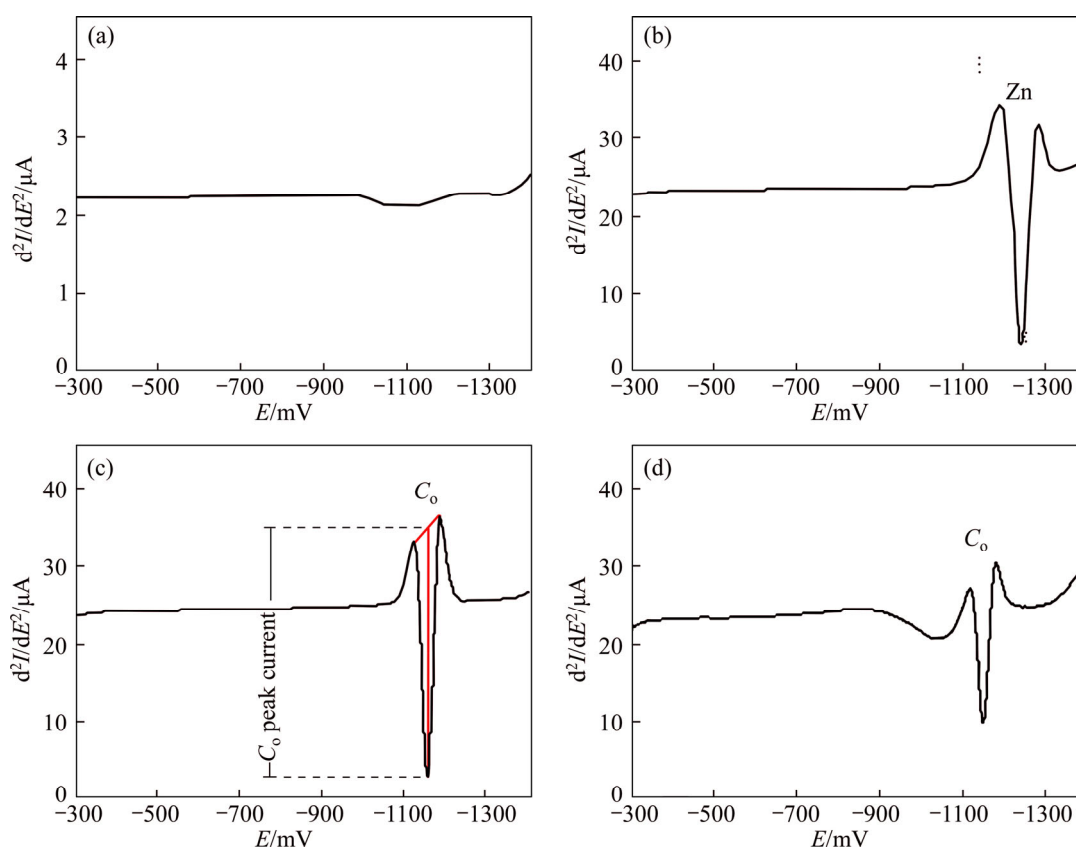


Figure 1 d^2I/dE^2 - E curves determined with several solutions (d^2I/dE^2 is electrochemical signal of Co(II) or Zn(II), namely the second derivatives): (a) Solution a containing 2.7×10^{-3} mol/L DMG, 0.48 mol/L $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer and 0.32 mol/L NaNO_2 ; (b) Solution b containing solution a with 5.2×10^{-2} mol/L Zn^{2+} ; (c) Solution d containing solution b with 6.0×10^{-2} mol/L EDTA and 2.0×10^{-8} mol/L Co^{2+} ; (d) Solution e containing solution a with 6.0×10^{-5} mol/L EDTA and 1.0 mL actual zinc electrolyte (after diluting 1000 times)

EDTA, generating eventually a highly sensitive and selective catalytic adsorptive wave of the Co(II) complex. Yet all of the complexes of other coexisting metal ions with EDTA can not produce polarographic waves across -300 to -1350 mV sweep voltage range, that is, no interference occurs during Co^{2+} determination.

The above results have shown that even without any pretreatment, EDTA can make Co^{2+} determination completely free of the influences of Zn^{2+} and other coexisting ions.

The concentration of impurity ions within the zinc electrolyte is several orders of magnitude lower than Zn^{2+} , therefore, the masking agent concentration can be tailored upon this. As mentioned above, in the Zn^{2+} chelate, the coordination ratio of EDTA onto Zn^{2+} is 1:1; a possible molar ratio under this value will obstruct EDTA to completely mask Zn^{2+} . The remaining Zn^{2+} still produces its polarographic wave, yet it might overlap with that of Co^{2+} , thus, the molar

ratio of $\text{EDTA}:\text{Zn}^{2+}$ should be above 1:1. However, we have experimentally observed that when the molar ratio is larger than approximately 1.5, the peak current (I_p) of Co^{2+} decreases with the increase of the ratio value, namely an excessive concentration of EDTA negatively influences the Co^{2+} determination (Figure 2(a)). The concentration of Zn^{2+} within the electrolyte is usually 2.2–2.9 mol/L, and in order to ensure that Zn^{2+} and other coexisting impurity ions are completely masked, an adequate concentration of EDTA is tailored only based on the maximum value (i.e., 2.9 mol/L). The $\text{EDTA}:\text{Zn}^{2+}$ molar ratio should 1:1, or slightly more; in this case, the Co^{2+} wave is not influenced by matrix Zn^{2+} and other coexisting impurity ions (Figure 1(d)). Therefore, the content of trace Co^{2+} within the zinc electrolyte can accurately be monitored by employing 3.0 mL of EDTA solution. Considering the possible effect of concentration fluctuation of matrix Zn^{2+} in the actual electrolytes, the Co^{2+} concentration should

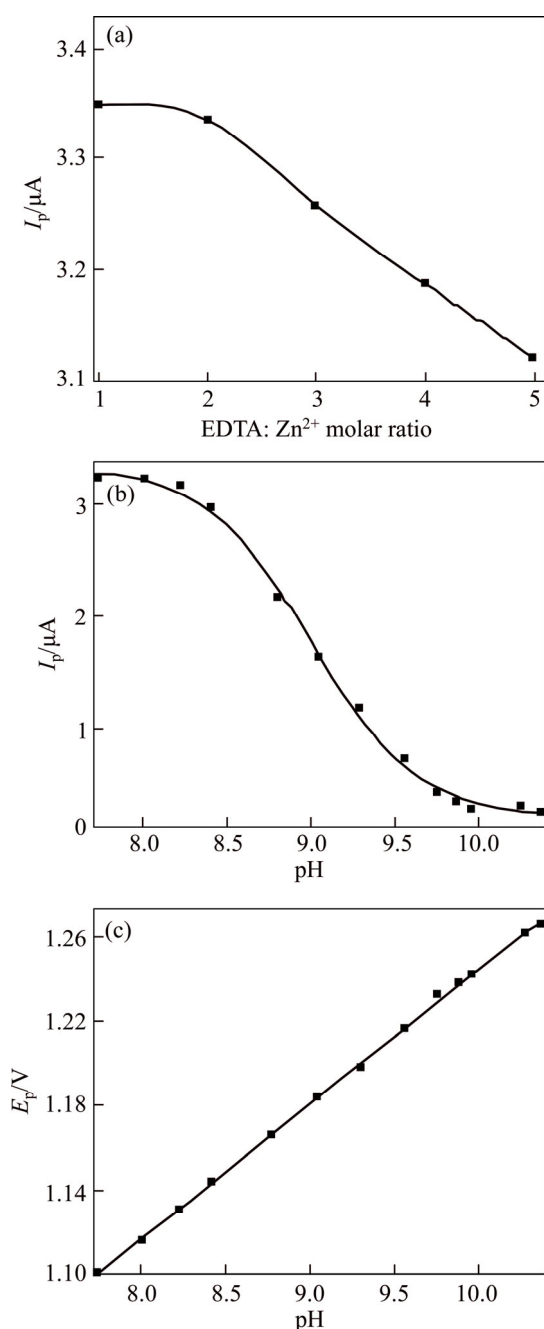


Figure 2 Influence of EDTA:Zn²⁺ molar ratio and pH on peak current I_p of second derivative wave of cobalt (a) and (b) as well as influence of pH on the peak potential E_p (c) (2.0×10^{-9} mol/L Co²⁺; 5.2×10^{-2} mol/L Zn²⁺)

be calculated using the standard addition method.

3.4 Influence of pH

The influences of acidity on the peak current (I_p) and peak potential (V_p) of Co²⁺ wave have been investigated across the 7.4–10.7 pH range by varying only the molar ratio of NH₃ and NH₄Cl within the buffer. The second derivative wave of Co²⁺ was determined according to “procedure”, and

the relationship between the I_p (or V_p) of Co²⁺ wave and the solution pH is shown in Figures 2(b) (or (c)). As depicted in Figure 2(c), the negative value of the V_p of Co²⁺ wave increases linearly with the pH increasing; hence, a linear relation equation is obtained: $V_p = -64.3 \text{ pH} - 602$ (mV) across 7.4–10.7 pH range. The results have indicated that H⁺ is involved in the electrode reaction. Figure 2(b) has shown the following phenomena: when the pH varies between 8.4 and 9.6, the I_p of Co²⁺ wave decreases in an approximately linear manner as the pH increases; at pH values <8.4 or >9.6, the I_p remains constant, but the I_p corresponding to pH <8.4 exhibits the most intense behavior, whereas the I_p of solution with pH >9.6 is the weakest. In this experiment, NH₃–NH₄⁺ buffer (pH=8.3) has been selected as a potential agent to control the acidity of the solution. As previously mentioned, besides being the conjugate acid of buffer, NH₄⁺ facilitates the absorption of the Co(II) complex onto the mercury electrode, thus triggering a very sensitive catalytic adsorptive wave of the Co(II) complex.

3.5 Influence of buffer concentration

In order to research the influence of NH₃–NH₄⁺ buffer concentration on the I_p of Co²⁺ wave, the second derivative waves of the Co²⁺ were determined according to “procedure”, by varying only the volume of the added buffer. The relationship between the I_p and the buffer concentration was shown in Figure 3(a). At concentrations under 0.45 mol/L, an approximately linear increasing trend has been monitored between the I_p of Co²⁺ wave and the concentration. Distinctively, the I_p maintains a constant trend at concentrations higher than 0.45 mol/L. Therefore, the adequate buffer concentration has been selected as 0.48 mol/L, that is, the volume of NH₃–NH₄Cl buffer added to the solution is 8.0 mL.

3.6 Influence of DMG concentration

DMG is present as a ligand in the system, the effect of DMG concentration on the I_p has been studied over 0.132 to 0.448 g/L range. The second derivative waves of Co²⁺ in some solutions were determined according to “procedure”, by varying only the volume of the added DMG solution. The relationship between the I_p and DMG concentration is shown in Figure 3(b). The figure has shown an

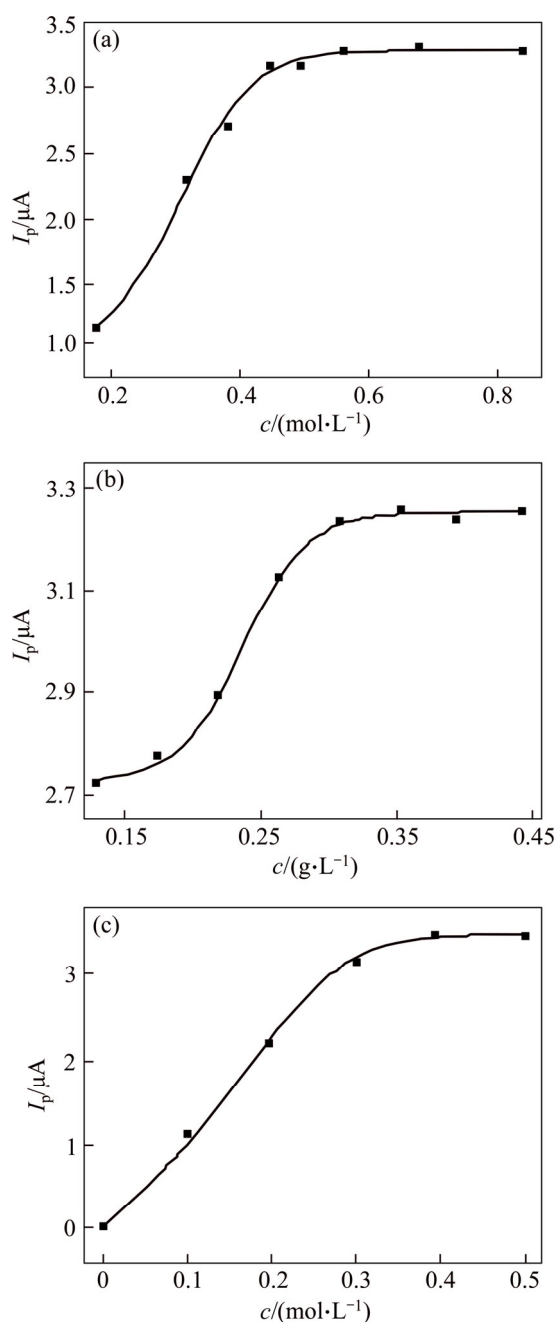


Figure 3 Influence of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (a), DMG (b) and NaNO_2 (c) concentrations on peak current I_p of second derivative wave of cobalt ($2.0 \times 10^{-9} \text{ mol/L Co}^{2+}$)

approximately linear increase of I_p with DMG concentration between 0.132 and 0.313 g/L range; the concentrations above 0.313 g/L have led to a constant I_p . However, through the experiment, we also observed that an excessive DMG ethanol solution added to the solution can adversely influence the I_p , weakening its signal. The concentration of ethanol into the test solution will increase with the volume of the added DMG ethanol solution. An excess of ethanol will generate

a competition between the Co^{2+} complex and ethanol for the adsorption onto the mercury electrode, therefore, the I_p will also be weakened [22]. At DMG concentrations above 0.31 g/L and room temperature, DMG will precipitate due to its low solubility in water. Thus, the only appropriate DMG concentration within the test solution should be 0.31 g/L, meaning that 1.4 mL DMG ethanol solution is required.

3.7 Influence of NaNO_2 concentration

NaNO_2 has a considerable influence on the method's sensitivity, its effect on the I_p of Co^{2+} wave has been investigated by changing its concentration and the result is depicted in Figure 3(c). The addition of NaNO_2 triggers a rapid increase of the I_p of the Co^{2+} wave. At concentrations $\geq 0.32 \text{ mol/L}$ (namely the added volume is $\geq 4.0 \text{ mL}$) the I_p is maintained intense and constant. Therefore, 4.0 mL of NaNO_2 solution was selected.

3.8 Influence of standing time of test solution before determination

The I_p can only be determined when the solution is steady, otherwise large errors arise and the reproducibility level is poor. A freshly prepared solution possessing the optimal conditions has been measured at different time. We have observed that, at standing time $< 5.0 \text{ min}$, I_p increases as the time passes by because the Co^{2+} complex formation requires some time. Across the 5–60 min range, I_p is strong and stable; yet at $> 60 \text{ min}$ the appearance of I_p becomes unsatisfactory, presumably because of the volatility of NH_3 in the base solution. Therefore, 5.0 min has been selected as the adequate standing time.

3.9 Calibration curve

The calibration curve has been recorded to verify the linear relationship between the I_p and Co^{2+} concentration in the presence of 0.26 mol/L Zn^{2+} under the optimal conditions. The I_p of the Co^{2+} wave is approximately proportional to its concentration within 1.0×10^{-10} – $3.2 \times 10^{-7} \text{ mol/L}$ range, a linear equation is obtained as following: $I_p = 325.9c - 1.71$ (nA), with a correlation coefficient of 0.9997, where c is Co^{2+} concentration in $n \text{ mol/L}$ (namely $n \times 10^{-9} \text{ mol/L}$). The detection limit, defined

as a concentration corresponding to a signal which is three times of the standard deviation of the blank peak current, equals 1.0×10^{-11} mol/L. The linear range and detection limit data are listed in Table 2 along with those of previously reported methods for Co^{2+} determination [2, 16, 17, 25]. By comparison with the other methods' data, ours display a wider linear range as well as a lower detection limit. In addition, our method can be easier than the other ones for actualizing the online detection of trace

Co^{2+} . It is obvious from the linear equation ($I_p=325.9c-1.71$) that the influence of the blank value (1.71 nA) is negligible in the linear range, namely the standard addition method may be used to determine the cobalt in real samples whose matrix components may be very different.

The polarographic curves of the blank containing all reagents (including zinc excess) and a part of the solutions with different concentrations of Co(II) are shown in Figure 4.

Table 2 Comparison of obtained results with selected previously reported data on voltammetric determination of Co^{2+} in zinc electrolyte[#]

Technique	Electrode	Linear range/ (mol·L ⁻¹)	Detection limit/ (mol·L ⁻¹)	Zn ²⁺ tolerance limit ^{##}	Reference
Differential pulse polarography	Dropping mercury electrode	1.0×10^{-7} – 5.0×10^{-6}	2.0×10^{-8}	2.3×10^5	[25]
Differential pulse polarography	Dropping mercury electrode	4.2×10^{-8} – 4.2×10^{-5}	5.5×10^{-9}	2.0×10^5	[16]
Differential pulse catalytic adsorptive stripping voltammetry	Hanging mercury drop electrode	1.0×10^{-10} – 1.0×10^{-8}	4.1×10^{-11}	1.4×10^7	[2,17]
Differential pulse catalytic adsorptive stripping voltammetry	Hanging mercury drop electrode	2.0×10^{-10} – 5×10^{-8}	2.4×10^{-11}	1.2×10^5	[17]
Second-derivative catalytic polarography	Dropping mercury electrode	1.0×10^{-10} – 3.2×10^{-7}	1.0×10^{-11}	3.0×10^7	This work

[#]: Data of linear range and detection limit were obtained under the condition without Zn^{2+} . ^{##}: Zn^{2+} tolerance limit is the mass times corresponding to the Co^{2+} within the solution.

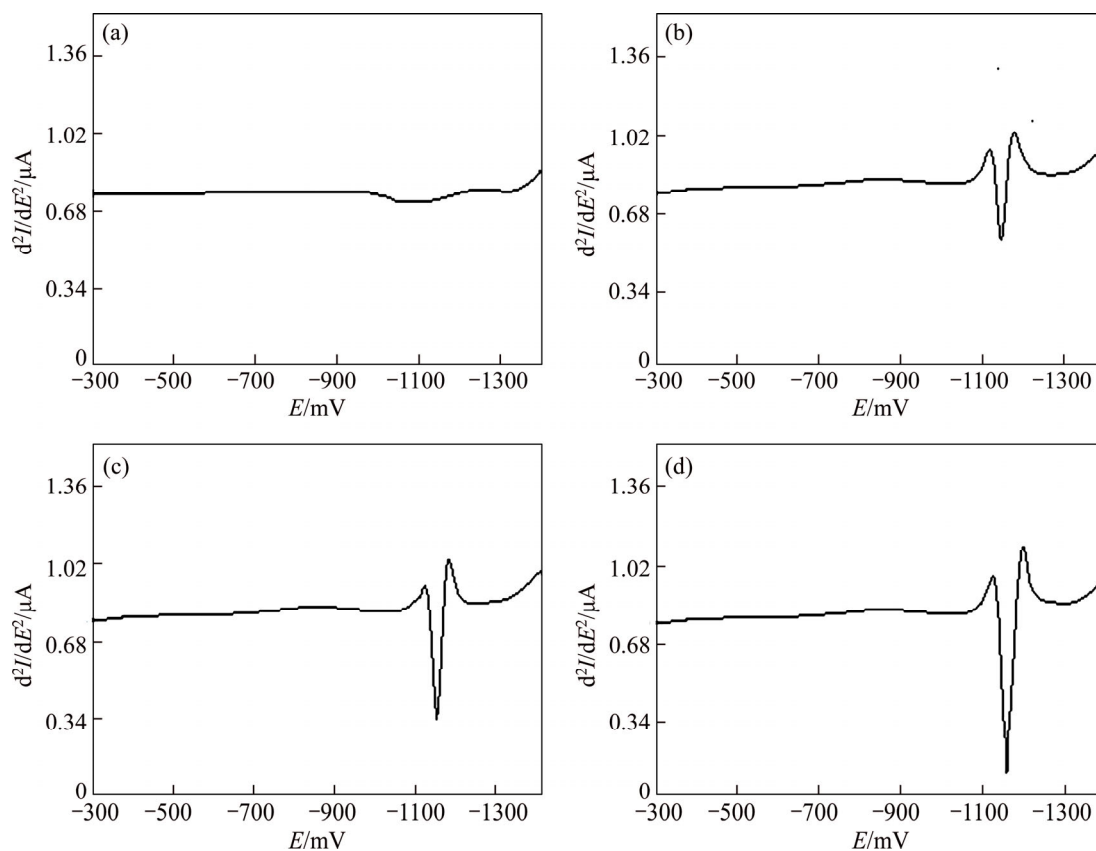


Figure 4 Polarographic curves of a part of solutions with different concentrations of Co(II) : (a) Blank solution containing 2.7×10^{-3} mol/L DMG, 0.48 mol/L $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer, 0.32 mol/L NaNO_2 , 0.26 mol/L Zn^{2+} and 0.30 mol/L EDTA; (b) Blank solution + 2×10^{-10} mol/L Co^{2+} ; (c) Blank solution + 4×10^{-10} mol/L Co^{2+} ; (d) Blank solution + 6×10^{-10} mol/L Co^{2+}

3.10 Interference

The influences of various ions, which may coexist in the test solution, on the determination of Co^{2+} within zinc electrolyte were examined. The results have shown that SO_4^{2-} , NO_3^- , ClO_3^- , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, $\text{HP}_2\text{O}_7^{3-}$, Br^- , Cl^- , F^- and NH_4^+ , Li^+ , Na^+ , K^+ , Sr^{2+} , Ba^{2+} do not interfere with Co^{2+} determination; the tolerance limits of other coexisting ions (5% relative error) are given below: 3.0×10^7 for Zn^{2+} and Al^{3+} , 1×10^6 for Mo^{6+} and W^{6+} , 56000 for Mn^{2+} , 50000 for Ca^{2+} , 21000 for Mg^{2+} , 14000 for Ge^{2+} and Hg^{2+} , 10000 for Sn^{4+} , 5100 for Si^{4+} , 5000 for Cu^{2+} , Pb^{2+} and Cd^{2+} , 4000 for Ni^{2+} and Bi^{3+} , 2400 for Fe^{3+} , 2000 for B^{3+} , 1600 for In^{3+} , 1200 for Sb^{3+} , 1100 for Ti^{3+} , Be^{2+} and Ag^+ , 1000 for As^{5+} , 150 for As^{3+} , 21 for Cr^{3+} , and 6 for V^{5+} .

3.11 Application of method

The actual zinc electrolytes were supplied by Zhuzhou Smelter Group Company Limited, Zhuzhou, China. According to the “procedure”, the Co^{2+} concentrations within the samples were determined using the standard addition method [31]. The calculation formula was

$$c_o = \Delta c (I_{P_o} / (I_P - I_{P_o})) \quad (8)$$

where c_o and Δc are the original concentration and increased concentration of the cobalt before and after the standard addition, respectively; I_{P_o} and I_P are the peak currents of the cobalt before and after the standard addition, respectively. It is obvious from the formula that the cobalt concentration can be determined by using only two measured data. As an example, the two measured data of a sample of new zinc electrolyte are shown in Figure 5. The results as compared with those of nitroso-R salt spectrophotography (NRS, a national standard method) have been listed in Table 3. The relative standard deviation (RSD) of this method is $\leq 2.7\%$; the absolute value of relative deviation between the results of two methods is $\leq 4.2\%$. The obtained results represent a fulfillment of the research's goals.

4 Conclusions

We report herein a highly selective method for the determination of Co^{2+} within zinc electrolytes. Under $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer medium, Co^{2+} reacts with DMG and NaNO_2 to produce an electrochemically

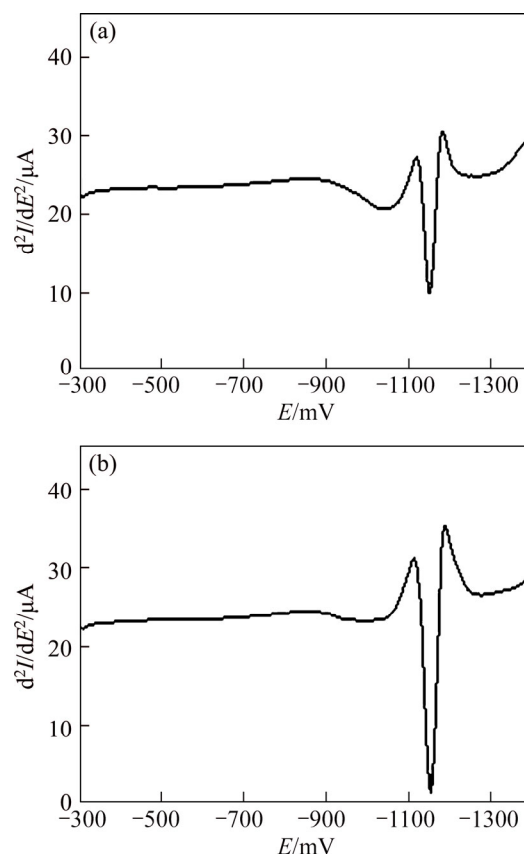


Figure 5 Voltammetric peaks of sample of new zinc electrolyte (after diluting 1000 times) obtained before (a) and after (b) standard addition (1.5×10^{-7} mol/L Co^{2+})

Table 3 Co^{2+} determination values as obtained by currently developed method and NRS as well as their comparison (six parallel determinations)

Sample	Value of current method/ ($\text{mg} \cdot \text{L}^{-1}$)	RSD of current method/%	Value of NRS/ ($\text{mg} \cdot \text{L}^{-1}$)	RD/%
Neutral supernatant solution	20.28	2.7	20.42	-0.69
New zinc electrolyte	0.43	1.5	0.45	-4.2
Cobalt removal solution	0.54	2.1	0.52	3.8

active complex which can form a very sensitive catalytic adsorptive derivative polarographic wave. The masking agent EDTA not only masks the high concentration of Zn^{2+} within the medium, eliminating completely its influence on trace Co^{2+} determination, but also masks most of the other coexisting metal ions. The proposed method has successfully been used to directly determine the trace Co^{2+} within actual zinc electrolytes without any pretreatment. The method's advantages are a

wide linear range, high sensitivity, excellent selectivity, readily available and less expensive reagents, being a promising and practical alternative from process control to online monitor of trace impurity Co^{2+} within zinc electrolytes during the hydrometallurgical process.

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中文导读

二阶导数催化极谱法选择性测定锌电解液中痕量钴

摘要: 本文报道了一个直接测定高浓度锌电解液中痕量钴的选择性方法。该方法基于测定 Co^{2+} 在滴汞电极表面与丁二酮及亚硝酸盐络合产生的催化吸附极谱的二阶导数波建立起来的。利用 $\text{NH}_3\text{-NH}_4\text{Cl}$ 缓冲剂, DMG 及 NaNO_2 组成的底液测定痕量钴时。由于 EDTA 的选择性掩蔽作用, 电解液中高浓度锌及任何其他金属离子的干扰都能完全排除。当 Co^{2+} 浓度在 $1.0 \times 10^{-10} \sim 3.2 \times 10^{-7} \text{ mol/L}$ 范围时, 与峰电流有良好的线性关系, 检出限为 $1.0 \times 10^{-11} \text{ mol/L}$, $\text{RSD} \leq 2.7\%$ 。将本法与亚硝基红盐显色法测定的结果进行了比较, 相对偏差的绝对值 $\leq 4.2\%$ 。本文提出的方法已成功用于实际锌电解液中痕量钴的测定。

关键词: 催化吸附伏安法; 高选择性掩蔽; 钴的测定; 锌电解液