



Simultaneous determination of trace Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} in zinc electrolytes by oscillopolarographic second derivative waves

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Abstract: Simultaneous determination of impurity metal ions in high concentration zinc solution is very important for zinc hydrometallurgy, and the purpose is to establish a method for determining the trace Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} in zinc electrolytes at the same time using the second derivative waves of single sweep oscillopolarography. Factors affecting the derivative waves of the ions were researched in a medium of dimethylglyoxime (DMG)–sodium citrate–sodium tetraborate. The results indicated that the interferences of a high concentration of Zn^{2+} and most other coexisting ions on the determination can be eliminated; when the Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} are in the ranges of 1×10^{-7} – 3×10^{-4} , 6×10^{-7} – 2×10^{-4} , 2×10^{-8} – 1×10^{-5} and 1×10^{-8} – 3×10^{-5} mol/L, respectively, the relationships between the peak currents of the second derivative waves and the concentrations are linear; the detection limits to determine the Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} are 8×10^{-8} , 2×10^{-7} , 6×10^{-9} and 4×10^{-9} mol/L, respectively. Without any sample pretreatment, the method was used to directly determine the trace Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} in actual zinc electrolytes with satisfactory results. The method is simple, sensitive and rapid.

Key words: zinc electrolyte; copper; cadmium; nickel; cobalt; second derivative wave

1 Introduction

In hydrometallurgy industry, the direct and simultaneous determination of trace amounts of Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} in high concentrations of Zn^{2+} solutions is still a challenging task for analysts so far [1]. The concentrations of impurity ions in the zinc electrolyte must be strictly controlled because their excessive concentrations, particularly Cu^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+} can cause a decrease in current efficiency and decrease the quality and morphology of cathode zinc [2]. Most removal methods in various hydrometallurgical plants are based on zinc powder replacement and chemical precipitation by adjusting the amount of reagents to be added depending on the impurity content. Therefore, a real-time and accurate monitoring of the contents of the impurities in the zinc electrolyte at the inlet and outlet of the relevant removal section is required, which can provide effective feedback information [3].

Traditional analytic methods to determine low

concentrations of heavy metals in zinc electrolyte are ICP-AES, GF-AAS, ICP-MS, etc. However, their instruments are expensive and require a good work environment. For ICP-AES, its matrix effect is notably serious; in particular, when the impurity concentration decreases, the accuracy of the determination results also decreases. Thus, it is difficult to use the methods in the rapid online detection in production fields. Electrochemical detection methods such as oscillopolarography and stripping voltammetry have been widely used to determine metal ions in complex matrices because of their low cost, high sensitivity, good selectivity and simple operation [4–6]. Among these methods, oscillopolarography uses a mercury drop electrode as the working electrode, which can be constantly updated; therefore, it is independent of its past history compared with other methods [7].

A high concentration of Zn^{2+} (130–170 g/L) in the electrolyte causes the matrix effect, decreases the sensitivity, and interferes with the determination; in particular, the proximity of the reduction potentials between Zn^{2+} and Co^{2+} makes the Co^{2+} signal easily

covered by Zn^{2+} [8]. Furthermore, the direct and simultaneous determination of certain impurity ions in the zinc electrolyte is not always feasible because of inadequate resolution. To solve the problems, many researchers have constantly improved the voltammetric methods to determine the trace impurity ions in zinc solutions [9–16]. However, the improved method cannot still be used to determine the trace cobalt in high concentrated zinc electrolytes or determine various impurity metals including cobalt in it at the same time.

In this study, an sensitive and accurate voltammetric method for determining the trace Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} in high concentrated zinc electrolytes at the same time has been established. In tetraborate buffer medium, the interference of Zn^{2+} with the determination of Co^{2+} can be eliminated completely under the complexation of sodium citrate.

2 Experimental

2.1 Apparatus and agents

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

The main agents were sodium hydroxide solution (2.0 mol/L), sodium tetraborate buffer (0.30 mol/L; the salt is dissolved by heating, and then the solution pH was adjusted to 9.3 with sodium hydroxide), sodium citrate solution (1.0 mol/L), DMG ethanol solution (11 g/L) prepared by dissolving 1.1 g DMG in 100 mL absolute ethanol, sulfuric acid solution (concentrated sulfuric acid mixed with water in a 1:2 ratio). The Zn^{2+} (2.6 mol/L), Cu^{2+} (0.010 mol/L), Cd^{2+} (0.010 mol/L), Co^{2+} (0.010 mol/L) and Ni^{2+} (0.010 mol/L) standard stock solutions were prepared by dissolving the corresponding sulphate in an appropriate amount of water, and diluted to the required concentration before use. The sulfates of the metal ions were guaranteed reagents, and other reagents were analytical reagents. The water was redistilled water.

2.2 Procedure

The testing process is divided into two steps: (1) An appropriate amount of the zinc electrolyte sample (or the metal standard solution to be measured and 1.0 mL ZnSO_4 solution) was transferred into a 10 mL volumetric flask; then, 0.15 mL DMG solution was added, mixed well; afterwards, 3.0 mL sodium citrate solution was added; after adjusting the solution to a weak acidity

(namely the color of methyl red just transformed from red to yellow) using sodium hydroxide, 4.0 mL sodium tetraborate buffer was added into the flask. The mixture was diluted to 10 mL with redistilled water and thoroughly mixed. The mixture was let to stand for 5 min and transferred into an electrolytic cell. The polarographic second derivative waves were recorded from -200 to -1400 mV (Fig. 1(a)), and the peaks of Cu^{2+} , Ni^{2+} and Co^{2+} appeared at approximately -366 , -1050 and -1180 mV, respectively. (2) After reading the data, 0.50 mL of sulfuric acid was added to the cell and mixed well. The second derivative wave was recorded from -400 to -800 mV using the continuous measurement function of the instrument (Fig. 1(b)), and the derivative wave of Cd^{2+} was obtained at approximately -600 mV. The parameters in the JP-303 system remained invariant during the testing process with a scanning rate of 0.5 V/s and a dropping mercury cycle of 9.0 s. The concentration of metallic ions was calculated using the standard addition method. In addition, all determinations were performed at $(20 \pm 2)^\circ\text{C}$, and all vessels were soaked with 10% nitric acid and washed with redistilled water.

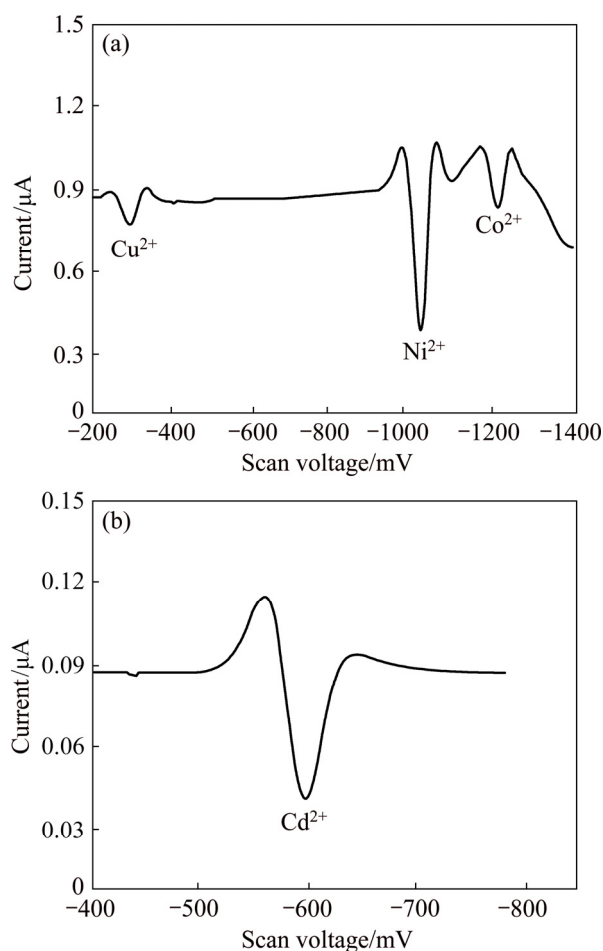
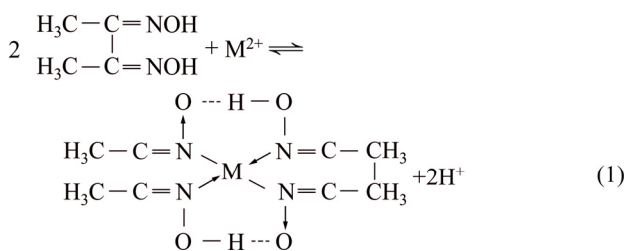


Fig. 1 Second derivative waves of Cu^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} solutions (1.0 mL zinc electrolyte + 0.15 mL DMG + 3.0 mL sodium citrate + 4.0 mL sodium tetraborate)

3 Results and discussion

According to the literatures and experiments [17,18], Cu^{2+} , Co^{2+} and Ni^{2+} can react with DMG with a coordination ratio of 1:2, as expressed in Eq. (1) (M^{2+} is Cu^{2+} , Co^{2+} or Ni^{2+}). From the equation, we observe that DMG is more likely to lose H^+ in an alkaline condition, so the reaction can more rapidly proceed.



However, Cd^{2+} has a low sensitivity in the alkaline condition because it hardly reacts with DMG, which does not satisfy the test requirement. Nonetheless, when the solution pH decreased to approximately 4.0, the sensitivity was remarkably improved.

Because of the difference between determining the Cu^{2+} , Co^{2+} and Ni^{2+} and determining the Cd^{2+} , we finally determined the test system: the Cu^{2+} , Co^{2+} and Ni^{2+} were determined in the alkaline buffer with DMG as a complexing agent; then, the Cd^{2+} was determined in the buffer whose $\text{pH}=4.0$.

3.1 Selection of conditions to determine Cu^{2+} , Co^{2+} and Ni^{2+}

3.1.1 Effect of pH on determining Cu^{2+} , Co^{2+} and Ni^{2+}

To select the optimum acidity, the effect of pH in the medium on the peak currents of the second derivative waves of Cu^{2+} , Co^{2+} and Ni^{2+} was studied in the range of 6.0 to 10.5. The pH was adjusted using sodium hydroxide. When the pH is less than 8.2, the Zn^{2+} wave appears at a more positive potential, which causes the overlap of the waves of Co^{2+} and Zn^{2+} . Because of the complexation of Zn^{2+} with citrate, the Zn^{2+} wave gradually moves towards a more negative potential with the increase of pH. When the pH is greater than 10.5, Zn^{2+} begins to precipitate because the hydroxide concentration is too large, and the peak currents of the ions to be measured decrease due to the co-precipitation. When the pH is 8.2–10.3, there is neither the polarographic derivative wave of zinc nor the hydroxide precipitation of zinc in the test interval, which facilitates the simultaneous on-line determination of the Cu^{2+} , Co^{2+} , Ni^{2+} . The relationships between the peak currents of Cu^{2+} , Co^{2+} , Ni^{2+} and the pH in the range of 8.2–10.3 are shown in Fig. 2. The peak current of Cu^{2+} increases with the increase of pH, whereas those of Co^{2+} and Ni^{2+} first increase and subsequently decrease, and at

approximately 8.8, reach their maximum values. It is obvious from Fig. 2 that the sensitivities of the Co^{2+} and Ni^{2+} are higher than that of the Cu^{2+} in the presence of DMG. In general, the Cu^{2+} concentration in the zinc electrolyte is much higher than that of the Co^{2+} and Ni^{2+} , therefore, to determine the three ions simultaneously, we finally selected $\text{pH}=9.3$ in the further study.

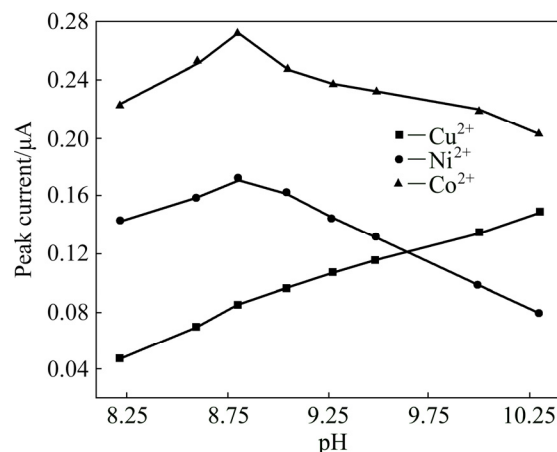
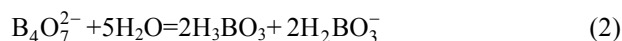


Fig. 2 Effect of pH on peak currents of Cu^{2+} , Co^{2+} and Ni^{2+} (Solution: 0.50 mL mixed metal ions (Cu^{2+} : 2.0×10^{-5} mol/L; Co^{2+} : 4.0×10^{-6} mol/L; Ni^{2+} : 2.0×10^{-6} mol/L) + 1.0 mL Zn^{2+} + 3.0 mL sodium citrate + 0.15 mL DMG + sodium hydroxide)

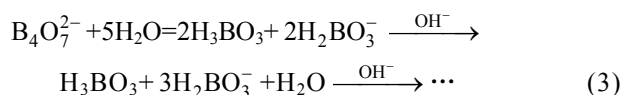
3.1.2 Choice of buffer system to determine Cu^{2+} , Co^{2+} and Ni^{2+}

Both $\text{NH}_3\text{-NH}_4\text{Cl}$ and sodium tetraborate may be used as buffers to control the solution pH at 9.3 because the negative logarithms of their relevant dissociation equilibrium constants ($\text{p}K_a$) are 9.25 and 9.24, respectively. However, on using DMG as the complexing agent to determine the Co^{2+} and Ni^{2+} in the zinc electrolyte under the alkaline condition, sodium tetraborate as the buffer is better than $\text{NH}_3\text{-NH}_4\text{Cl}$. When the Co^{2+} and Ni^{2+} in $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution are determined using DMG, the reduction potential of Zn^{2+} will be more negative due to the complexation of the Zn^{2+} and ammonia, which weakens the effect of Zn^{2+} on the determination of Co^{2+} and Ni^{2+} but cannot completely eliminate the effect of a large quantity of Zn^{2+} [19–22]. However, on determining the Cu^{2+} , Co^{2+} and Ni^{2+} in the buffer solution of sodium tetraborate, the Zn^{2+} does not produce any polarographic derivative wave in the range of scan interval. It is a major advantage for determining the impurities in the zinc electrolyte, particularly the Co^{2+} and Ni^{2+} . Thus, we selected sodium tetraborate as the buffer. The principle to form the buffer system by the hydrolysis of sodium tetraborate may be shown by Eq. (2).



It is obvious from Eq. (2) that the hydrolysis of

sodium tetraborate forms a buffer solution consisting of H_3BO_3 and NaH_2BO_3 . The molar ratio of conjugated acid to conjugated base is 1:1. Therefore, when the buffer concentration is constant, the buffer capacity is the largest, and the solution pH is 9.24, which equals $\text{p}K_{\text{a}1}$. The pH can be adjusted to 9.3 using sodium hydroxide. In addition, it is obvious from Eq. (3) that the addition of sodium hydroxide not only adjusts the buffer solution pH but also increases the solubility of sodium tetraborate.



3.1.3 Effect of sodium tetraborate concentration

To examine the effects of the buffer concentration on the peak currents of Cu^{2+} , Co^{2+} , and Ni^{2+} waves, their polarographic derivative waves in the test solutions were determined by only changing the volume of the added buffer. The results are shown in Fig. 3. The peak currents of the Cu^{2+} and Ni^{2+} are not affected by the sodium tetraborate concentration, and the peak current of the Co^{2+} increases with its increase. When the added sodium tetraborate volume exceeds 3.4 mL, the peak current is substantially constant. In addition, by the comparison of Fig. 2 and Fig. 3, it is obvious that when the concentrations of the ions to be measured and the solution pH are constant, all of the peak currents of the ions decrease slightly after adding sodium tetraborate to the solution. Therefore, the volume of the added sodium tetraborate buffer must be constant, and is selected as 4.0 mL.

3.1.4 Effect of sodium citrate concentration

To select the best amount of sodium citrate, the effect of its concentration on the derivative waves of Cu^{2+} , Co^{2+} and Ni^{2+} was studied by only changing its

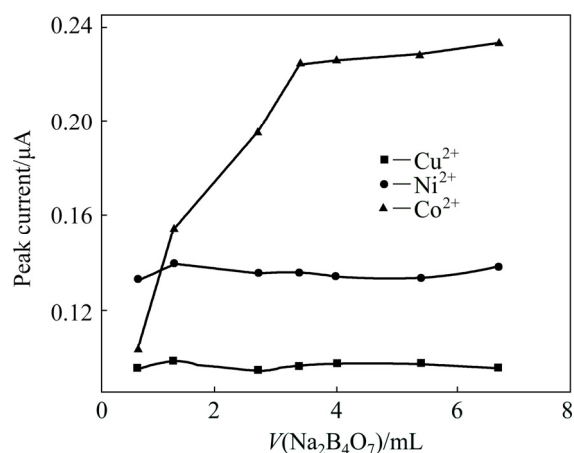


Fig. 3 Effect of sodium tetraborate volume on peak currents of Cu^{2+} , Co^{2+} and Ni^{2+} (Solution: 0.50 mL mixed metal ions (Cu^{2+} : 2.0×10^{-5} mol/L; Co^{2+} : 4.0×10^{-6} mol/L; Ni^{2+} : 2.0×10^{-6} mol/L) + 1.0 mL Zn^{2+} + 3.0 mL sodium citrate + 0.15 mL DMG + sodium tetraborate)

added volume in the 1.0–5.0 mL range. The relationships between the peak currents and the added volume are shown in Fig. 4. Sodium citrate was used as a zinc-complexing agent in this study. When the volume of sodium citrate was less than 3.0 mL, a white precipitate formed in the solution, which was produced from the hydrolysis of Zn^{2+} , and the peak currents of metal ions to be measured decrease due to their co-precipitation. However, when the added volume was too large, the peak currents would also decrease due to the complexation of the metal ions with citrate. It is obvious from Fig. 4 that the appropriate volume of sodium citrate added to the test solution is 3.0 mL. Therefore, for all subsequent parts in the study, 3.0 mL sodium citrate solution was used.

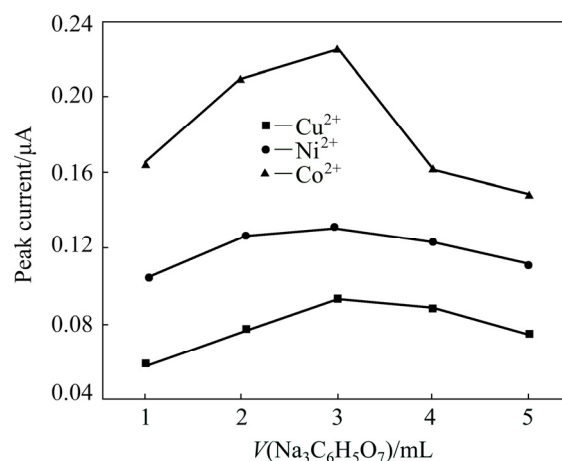


Fig. 4 Effect of sodium citrate volume on peak currents of Cu^{2+} , Co^{2+} and Ni^{2+} (Solution: 0.50 mL mixed metal ions (Cu^{2+} : 2.0×10^{-5} mol/L; Co^{2+} : 4.0×10^{-6} mol/L; Ni^{2+} : 2.0×10^{-6} mol/L) + 1.0 mL Zn^{2+} + 4.0 mL sodium tetraborate + 0.15 mL DMG + sodium citrate)

3.1.5 Effect of DMG concentration

DMG is present as a ligand in the system. The effects of DMG concentration on the second derivative waves of the Cu^{2+} , Co^{2+} and Ni^{2+} were studied by only changing the volume of the added DMG solution. The relationship between the peak current and the DMG volume is shown in Fig. 5. The increase of DMG concentration causes the peak current variation, and the variation trends of peak currents of the three ions are similar. When the DMG volume is lower than 0.05 mL, their peak currents rapidly increase with the increase of DMG concentration, and subsequently slowly increase. When the added DMG volume is higher than 0.15 mL (0.12 mL for the Ni^{2+}), the peak currents reduce instead because too much ethanol in the test solution, which is introduced from the added DMG ethanol solution, competes with the ion complexes for the adsorption on the mercury electrode. Therefore, the peak current will become weak [17]. Therefore, 0.15 mL DMG ethanol solution should be selected.

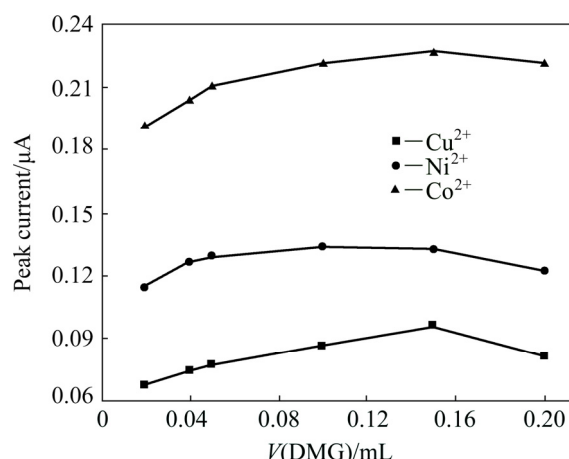


Fig. 5 Effect of DMG volume on peak currents of Cu^{2+} , Co^{2+} and Ni^{2+} (Solution: 0.50 mL mixed metal ions (Cu^{2+} : 2.0×10^{-5} mol/L; Co^{2+} : 4.0×10^{-6} mol/L; Ni^{2+} : 2.0×10^{-6} mol/L)+ 1.0 mL Zn^{2+} +4.0 mL sodium tetraborate + 3.0 mL sodium citrate + DMG)

3.2 Selection of conditions to determine Cd^{2+}

Cd^{2+} cannot produce the complex adsorption wave in the test solution because it does not react with DMG, so it cannot be determined simultaneously with Cu^{2+} , Co^{2+} , Ni^{2+} in the alkaline medium. However, in a weak acidic solution, Cd^{2+} can produce a sensitive second derivative wave. Therefore, the Cd^{2+} in zinc electrolyte can be determined just choosing a suitable acidity and buffer system.

3.2.1 Effect of pH on determining Cd^{2+}

The experiment has found that the sensitivity of Cd^{2+} derivative wave is particularly affected by the Zn^{2+} in the alkaline buffer. For example, when the concentration of the Zn^{2+} is 0.26 mol/L, the cadmium peak current is reduced by approximately 100 times. However, the cadmium current in acidic solutions are hardly affected by zinc. In the experiment, the sulfuric acid was used to adjust the pH, and we studied the change of the Cd^{2+} peak current in the range of pH 3.3–5.5 (Fig. 6). The peak current first increases and subsequently decreases with the increase of pH; when pH=4.0, the maximum peak current is obtained.

3.2.2 Choice of buffer system to determine Cd^{2+}

If a proper amount of sulfuric acid is added to the solution after determining the Cu^{2+} , Co^{2+} and Ni^{2+} , the citrate (Cit^{3-}) may be converted into an amphoteric acid-base compound, namely bi-hydrogen citrate (H_2Cit^-) buffer. Citric acid (H_3Cit) as the conjugated acid is a weak acid containing three protons, and its ionization equilibriums and the negative logarithms of the equilibrium constants are as follows:

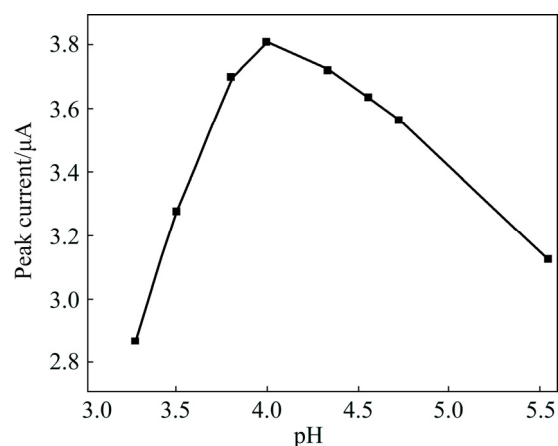
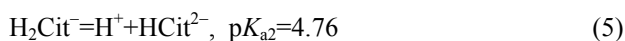
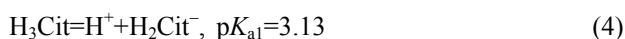
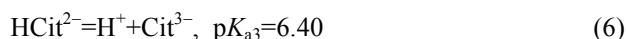


Fig. 6 Effect of pH on peak current of Cd^{2+} (Solution: 1.0 mL Cd^{2+} (6.0×10^{-5} mol/L) + 1.0 mL Zn^{2+} + 4.0 mL sodium tetraborate + 3.0 mL sodium citrate + 0.15 mL DMG + sulfuric acid)



According to principles of the material balance and the acid-base dissociation equilibrium, the formulas to calculate the distribution fractions of the four forms of citrate existing in the solution can be obtained. The formulas and the calculation results at pH=4.0 are as follows:

$$\delta_{\text{H}_3\text{Cit}} = \frac{[\text{H}^+]^3}{([\text{H}^+]^3 + [\text{H}^+]^2 K_{a1} + [\text{H}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3})} = 0.103 \quad (7)$$

$$\delta_{\text{H}_2\text{Cit}^-} = \frac{[\text{H}^+]^2 K_{a1}}{([\text{H}^+]^3 + [\text{H}^+]^2 K_{a1} + [\text{H}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3})} = 0.764 \quad (8)$$

$$\delta_{\text{HCit}^{2-}} = \frac{[\text{H}^+] K_{a1} K_{a2}}{([\text{H}^+]^3 + [\text{H}^+]^2 K_{a1} + [\text{H}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3})} = 0.133 \quad (9)$$

$$\delta_{\text{Cit}^{3-}} = \frac{K_{a1} K_{a2} K_{a3}}{([\text{H}^+]^3 + [\text{H}^+]^2 K_{a1} + [\text{H}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3})} = 5.29 \times 10^{-4} \quad (10)$$

It is obvious that when pH=4.0, the amphoteric substance, H_2Cit^- is the main form of existence, which can form a very good buffer system. The sensitive and stable peak current of Cd^{2+} may be determined in the buffer system. At pH=9.3, the calculation result of the distribution fraction of the trivalent anion, namely the citrate (Cit^{3-}) is 1.00. This shows that the citrate in the test solution to determine the Cu^{2+} , Co^{2+} and Ni^{2+} exists completely in the form of Cit^{3-} . Therefore, before determining the cadmium, a proper amount of the sulfuric acid should be added to the solution to form the buffer system whose pH=4.0. The experiment has shown that when 0.50 mL of the sulfuric acid is added to the solution, the desired pH is obtained.

3.3 Linear ranges, detection limits and repeatability of method

Under the optimal conditions, the linear relationships between the peak currents and the metal concentrations in the presence of 0.26 mol/L Zn²⁺ were researched. The results indicate that the current–concentration relationships are linear in the concentration ranges of 1×10⁻⁷–3×10⁻⁴, 6×10⁻⁷–2×10⁻⁴, 2×10⁻⁸–1×10⁻⁵, and 1×10⁻⁸–3×10⁻⁵ mol/L for Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺, respectively. The equations to indicate the linear relationships among the Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺ peak currents (*I_p*) and the concentrations (*C*) are *I_p*=13.5*C*(Cu²⁺)+0.135, *I_p*=16.1*C*(Cd²⁺)+0.392, *I_p*=1.56*C*(Ni²⁺)+0.011 and *I_p*=1.32*C*(Co²⁺)+0.016, respectively. The detection limits (3σ) of the Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺ are 8×10⁻⁸, 2×10⁻⁷, 6×10⁻⁹ and 4×10⁻⁹ mol/L, respectively. The correlation coefficients are 0.9990, 0.9995, 0.9991 and 0.9992, respectively. Six repeated determinations have shown that the relative standard deviations for 5×10⁻⁷ mol/L Cu²⁺, 1×10⁻⁶ mol/L Cd²⁺, 2×10⁻⁷ mol/L Ni²⁺ and 2×10⁻⁷ mol/L Co²⁺ are 1.2%, 0.73%, 1.2% and 1.6%, respectively, namely the method is of satisfactory precision.

3.4 Interference study

Special attention was paid to the interference of Zn²⁺. It was observed that Zn²⁺ whose concentration was lower than 0.30 mol/L did not affect the determination. The interference of other foreign ions was studied for a solution that contained 0.26 mol/L Zn²⁺, 5×10⁻⁷ mol/L Cu²⁺, 1×10⁻⁶ mol/L Cd²⁺, 2×10⁻⁷ mol/L Ni²⁺ and Co²⁺ by adding the foreign ions to the solution. The results show that SO₄²⁻, HSO₄⁻, B₄O₇²⁻, H₂BO₃⁻, HBO₃⁻, Cit³⁻, HCit²⁻, H₂Cit⁻, PO₄³⁻, P₂O₇⁴⁻, HP₂O₇³⁻, Br⁻, Cl⁻, F⁻ and NH₄⁺, Li⁺, Na⁺, K⁺, Sr²⁺, Ba²⁺ do not interfere with the determination. The tolerance limits of other coexisting ions (namely the mass times corresponding to 0.2 mg/L of Cu²⁺, Cd²⁺ and 0.04 mg/L of Ni²⁺, Co²⁺ (5% relative error)) are, respectively, Al³⁺, W(VI), Mo(VI) (90000 and 38000), Mn²⁺ (48000 and 20000), Ca²⁺ (39000 and 16000), Mg²⁺ (11500 and 4900), Ge²⁺, Hg²⁺ (9500 and 4100), Sn(IV) (8000 and 3100), Si(IV) (5200

and 2100), Bi³⁺ (3800 and 1600), As(V) (950 and 400), As³⁺ (100 and 45), Fe³⁺ (230 and 95), In³⁺ (200 and 75), Sb³⁺ (13 and 6), Ti³⁺, Be²⁺, Ag⁺ (10 and 4), Cr³⁺, V(V) (9 and 4). It is obvious that the method to determine the Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺ in the zinc electrolyte is of satisfactory selectivity.

3.5 Application of method

The proposed method was applied to determining the Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺ in some actual zinc electrolytes from Zhuzhou Smelter Group Company Limited, Zhuzhou, China, which were collected at the third purification process section at different time. To quantify the four ions, 1.0 mL of zinc electrolytes was added to the test solution. Three parallel determinations were performed for each sample. The results are shown in Table 1. The recoveries are 96.0%–104%, the accuracy is satisfactory.

4 Conclusions

1) A new method to determine the Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺ in zinc electrolytes at the same time is offered. In a solution whose pH=9.3, the complexes formed by the reactions of Cu²⁺, Ni²⁺, Co²⁺ with DMG will produce sensitive second derivative waves; however, under the action of citrate anion, Zn²⁺ does not produce any derivative wave in the scan interval, which may completely eliminate the interference of the Zn²⁺ with the determination of the Ni²⁺ and Co²⁺. In addition, a sensitive derivative wave of Cd²⁺ will emerge in a weak acidic solution (pH=4.0). Therefore, the Cu²⁺, Ni²⁺ and Co²⁺ can be determined in the alkaline solution containing DMG and Cit³⁻, and the Cd²⁺ can be determined under the acidic condition, using sodium tetraborate and sodium bi-hydrogen citrate solutions to control the pH under the alkaline and acidic conditions, respectively.

2) The method has satisfactory precision and accuracy, is simple, requires a low cost, and can quickly and directly achieve the simultaneous determination of Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺.

Table 1 Results to determine Cu²⁺, Cd²⁺, Ni²⁺ and Co²⁺ in actual zinc electrolytes collected thrice

Sample No.	Added concentration/(mg·L ⁻¹)				Determined average concentration/(mg·L ⁻¹)				Recovery/%			
	Cu ²⁺	Cd ²⁺	Ni ²⁺	Co ²⁺	Cu ²⁺	Cd ²⁺	Ni ²⁺	Co ²⁺	Cu ²⁺	Cd ²⁺	Ni ²⁺	Co ²⁺
1	0	0	0	0	0.125	0.921	0.038	0.125	103	104	102	99.0
	0.200	0.700	0.050	0.100	0.331	1.650	0.089	0.224				
2	0	0	0	0	0.093	0.692	0.046	0.154	97.0	103	96.0	98.0
	0.200	0.700	0.050	0.100	0.287	1.416	0.094	0.252				
3	0	0	0	0	0.246	0.834	0.072	0.068	101	99.1	104	102
	0.200	0.700	0.050	0.100	0.448	1.528	0.124	0.170				

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用示波极谱二阶导数波同时 测定锌电解液中微量铜、镉、镍、钴

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摘要: 同时测定高浓度锌电解液中多种杂质金属离子对湿法炼锌非常重要, 旨在建立一种用单扫描示波极谱二阶导数波同时测定锌电解液中微量铜、镉、镍、钴的新方法。研究这四种金属离子在丁二酮肟-柠檬酸钠-四硼酸钠介质中极谱导数波的影响因素。结果表明: 高浓度 Zn^{2+} 和其他大多数共存离子不干扰 Cu^{2+} 、 Cd^{2+} 、 Ni^{2+} 和 Co^{2+} 的测定。锌电解液中 Cu^{2+} 、 Cd^{2+} 、 Ni^{2+} 和 Co^{2+} 的浓度分别在 $1 \times 10^{-7} \sim 3 \times 10^{-4}$ 、 $6 \times 10^{-7} \sim 2 \times 10^{-4}$ 、 $2 \times 10^{-8} \sim 1 \times 10^{-5}$ 和 $1 \times 10^{-8} \sim 3 \times 10^{-5}$ mol/L 范围时, 其二阶导数波峰电流与浓度呈线性关系。 Cu^{2+} 、 Cd^{2+} 、 Ni^{2+} 和 Co^{2+} 的检出限分别为 8×10^{-8} 、 2×10^{-7} 、 6×10^{-9} 和 4×10^{-9} mol/L。该方法无需任何预处理直接测定锌电解液中的 Cu^{2+} 、 Cd^{2+} 、 Ni^{2+} 和 Co^{2+} , 结果令人满意。该方法简便、灵敏、快速。

关键词: 锌电解液; 铜; 镉; 镍; 钴; 二阶导数波

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