CONCENTRATION AND DETERMINATION OF COBALT MICROIMPURITIES IN NICKEL SALTS BY FILM POLAROGRAPHY

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We have demonstrated the possibility of concentrating and determining cobalt microimpurities as a poorly soluble inner complex of trivalent cobalt with nitrosonaphthols (CoR_3) [1]. In the present work, this method has been used for the analysis of nickel salts. The ON-101 and 7-77 4/V Hungarian recording polarographs and the 02-TsLA oscillographic polarograph were used. The preparation of the working graphite electrode has been described before [2].

Figure 1 gives the polarization curves for the dissolution of the compound between trivalent cobalt and 2-nitroso-1-naphthol. The solutions contained increasing amounts of nickel salt. The first peak on the curve corresponds to the reagent, and the second is due to reduction of cobalt. The latter decreases with increase in the nickel content of the solution. The sensitivity of the determination is slightly improved by increasing the concentration of the reagent.

Figure 2 shows the dependence of the maximum electrochemical reduction current for CoR_3 on the concentration of divalent cobalt ions in a solution containing nickel. The sensitivity of the cobalt determination in the presence of 1.6 g-ion/liter divalent nickel amounts to 2×10^{-7} g-ion/liter divalent cobalt; in a solution containing 0.4 g-ion/liter Ni^{2+}, 5×10^{-8} g-ion/liter divalent cobalt was recorded, which corresponds to a sensitivity of 2×10^{-4}% cobalt in the nickel salt. The results obtained for the reproducibility of the determinations were similar to those described earlier [1].

The distortion of the rising branch of the polarogram for cobalt, which results from superposition of the cathodic current of the reagent, can be avoided if the electrode is held at -0.55 V before the curve is recorded. This method was used when the polarization curves shown in Fig. 2 were recorded.

To improve the sensitivity of cobalt determination in nickel, it is advisable to extract the nickel thiocyanate–diantipyrylmethane compound with chloroform [3].

Specific quantities of cobalt were added to the analyzed sample of nickel salt, the nickel was removed by extraction, and the cobalt concentration was determined by the method described above. Figures 3 and 4 give the respective polarization curves for the electrochemical reduction of CoR_3. The maximum cathodic current is proportional to the divalent cobalt concentration.

A 0.5-g sample of basic nickel carbonate, weighed to an accuracy of 0.01 g, was dissolved in 2-ml hydrochloric acid. The solution was diluted to 20 ml with water and transferred to a separating funnel. A 5-ml portion of 5-mole/liter ammonium thiocyanate solution and 0.2 ml 0.05-mole/liter diantipyrylmethane (DM) solution in 0.5-mole/liter hydrochloric acid were added, and the mixture was shaken for 1.5 min with 2 ml chloroform. The extraction was repeated, adding 0.3 ml ammonium thiocyanate and 0.3 ml DM solution. All the chloroform extracts were collected in a porcelain crucible, evaporated to dryness on a water bath, ashed, and heated for 1 h at 600°C in a muffle furnace.

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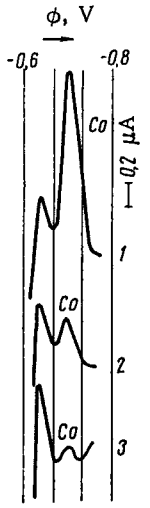

Fig. 1

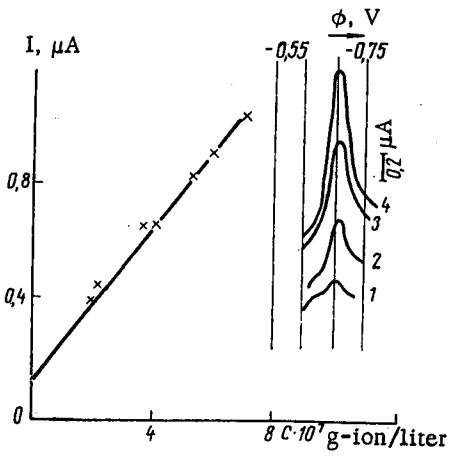

Fig. 2

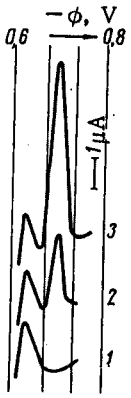

Fig. 3

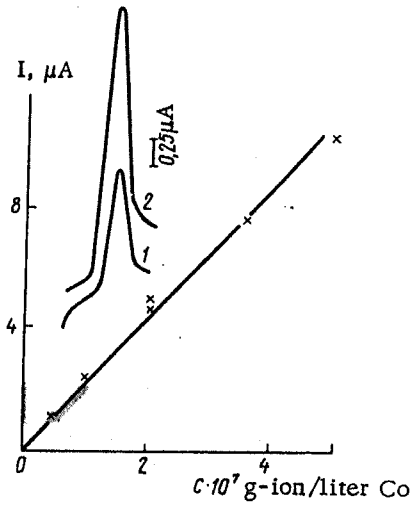

Fig. 4

Fig. 1. Polarization curves for electrochemical reduction of compound CoR_3, concentrated from a solution of 1.5 mole/liter NH_4OH + 0.1 mole/liter NH_4Cl + 4 × 10^{-6} mole/liter 2-nitroso-1-naphthol + 4 × 10^{-7} g-ion/liter Co(II). 1) Without nickel; 2) 0.2 g-ion/liter Ni(II); 3) 0.4 g-ion/liter Ni(II).

Fig. 2. Dependence of maximum electrochemical reduction current for CoR_3 on concentration of divalent cobalt ions in solution and corresponding polarization curves. Composition of solutions: 1.6 g-ion/liter Ni(II) + 1.5 mole/liter NH_4OH + 0.1 mole/liter NH_4Cl + 2 × 10^{-5} mole/liter 2-nitroso-1-naphthol. 1) Without Co(II); 2) 2 × 10^{-7} g-ion/liter Co(II); 3) 4 × 10^{-7} g-ion/liter Co(II); 4) 6 × 10^{-7} g-ion/liter Co(II).

Fig. 3. Polarization curves for reduction of CoR_3: 1) without cobalt; 2) 2 × 10^{-7} g-ion/liter Co; 3) 5 × 10^{-7} g-ion/liter Co.

Fig. 4. Dependence of maximum electrochemical reduction current for CoR_3 on concentration of cobalt ions in nickel carbonate and corresponding oscillograms: 1) 5 × 10^{-8} g-ion/liter Co(II); 2) 1 × 10^{-7} g-ion/liter Co(II).

After cooling the crucible, 0.5 ml concentrated hydrochloric acid was added to the dry residue, and the walls were carefully wetted while gently heating the crucible on an electric plate until the residue dissolved completely. The volume was made up to 25 ml with the supporting electrolyte consisting of 1.5 mole/liter NH_4OH + 0.1 mole/liter NH_4Cl, and the solution was transferred to the electrolyzer.

Dissolved oxygen was removed by passing nitrogen through the solution for 10 min. To the analyzed solution was added 0.5 ml 1 × 10^{-4} mole/liter 2-nitroso-1-naphthol solution, and electrolysis was continued for 5 min at −0.45 V.

The potential of the electrode was moved to −0.55 V, the potential sweep was actuated, the polarization curve was recorded between −0.55 and −0.90 V, and the maximum electrochemical reduction current of CoR_3 was measured (ϕ_m = −0.75 V). The cobalt content of nickel was determined by the method of additions. The error in a single determination of 4 × 10^{-7} g-ion/liter Co(II) with n = 10, α = 0.95, and t = 2.3 [4] amounts to 14.2%. The sensitivity of the analysis for Co(II) is 5 × 10^{-8} g-ion/liter, which amounts to ~1 × 10^{-5}% for a sample of 0.5 g basic nickel carbonate.

LITERATURE CITED

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