Determination of cobalt(II) by controlled potential coulometry

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Dedicated to Professor S. Stankoviansky on the occasion of his 65th birthday

The determination of Co(II) in the presence of Fe(II), Ni(II), Mn(II), Cr(III), and Zn(II) by controlled potential coulometry is described. The method is based on the oxidation of tris(1,10-phenanthroline) cobalt(II) complex at $+0.40 - +0.50$ V *vs.* saturated silver chloride electrode at platinum and glassy carbon electrodes in a supporting electrolyte containing an excess of the complexing agent at pH 3.0—4.8. Fe(III) causes interference. The determination of the quantity of electricity passed using the log i *vs.* t plots eliminates the need for an integrator. The estimate standard deviation for the determination of 2.0×10^{-8} g-ion Co(II) is 1.6%.

Various new applications of cobalt have provoked an increasing interest in the analytical chemistry of this element and in new methods for its determination in technological and biological materials [1]. Coulometry provides precise, rapid, and simple determination of many substances without the need for standard titrants.

The complexometric determination of cobalt(II) by constant current coulometric back titrations with electrogenerated Cd(II) (dual-intermediate titrations) [2] and La(III) ions [3] was described. *Patriarche* [4, 5] established cobalt by titration with coulometrically generated bromine after separation of its 8-hydroxyquinoline chelate. Co(II) was oxidized coulometrically to Co(III) using either Mo(V) in ammoniacal medium [6] or ferricyanide in the presence of glycine in alkaline medium [7] as intermediate reagents. More selective determination of cobalt in the presence of nickel by controlled potential coulometric reduction at a mercury pool electrode was described in [8]. Microamounts of ^{60}Co in nitric acid were determined by controlled potential coulometry at a stationary amalgamated platinum electrode [9].

The present work describes the determination of Co(II) by controlled potential coulometric oxidation of its tris(1,10-phenanthroline) complex.

Cobalt(II) and 1,10-phenanthroline (phen) may lead to the formation of the following complexes: $[Co(phen)]^{2+}$, $[Co(phen)_2]^{2+}$, and $[Co(phen)_3]^{2+}$, for which the logarithms of the overall stability constants are 7.0, 13.7, and 20.1, respectively [10]. Assuming that there is a sufficient excess of the complexing agent and the solution is not strongly acid then $[Co(phen)_3]^{2+}$ is practically the only species present. The formal oxidation-reduction potentials (*vs.* normal hydrogen electrode) are the following [11]:

$$[Co(phen)_3]Cl_3 + e = [Co(phen)_3]Cl_2 + Cl^- \qquad E_0' = 0.37 \text{ V},$$

$$[Co(phen)_3](ClO_4)_3 + e = [Co(phen)_3](ClO_4)_2 + ClO_4^- \qquad E_0' = 0.42 \text{ V}.$$

Voltammetric and chronopotentiometric investigations have shown that the system $[CoL_3]^{3+} + e = [CoL_3]^{2+}$ (where L is 2,2′-bipyridine or 1,10-phenanthroline) is electrochemically fairly reversible at the platinum [12] and at various carbon electrodes [13—15].

Experimental

Twice distilled water was used for the preparation of all solutions. 0.01 M-$CoCl_2$ stock solutions were prepared from recrystallized $CoCl_2 \cdot 6H_2O$ (reagent grade, Lachema, Brno), and were standardized by potentiometric titration using ferricyanide [16]. Lower concentration solutions were prepared by dilution. Other chemicals used were reagent grade (Lachema, Brno). Micropipettes were used to take aliquots of the cobalt standard solutions for analysis. The supporting electrolytes were prepared from 0.2—0.8 M acetic (or monochloroacetic) acid containing 0.01—0.1 M-1,10-phenanthroline, the pH of which was adjusted to 3.0—4.8 with NaOH and subsequently diluted to give 0.1—0.4 M solutions in acetate (chloroacetate) ion.

A three-electrode polarograph OH-102 (Radelkis) was used for the voltammetric measurements as well as for constant potential coulometric microdeterminations with simultaneous recording of *i vs. t* curves. The more concentrated samples were determined using an OH-404 coulometer (Radelkis).

The electrolysis cell with a platinum working electrode consisted of a 4 × 6 cm weighing bottle equipped with a 3 × 3 cm platinum gauze cylinder. The tip of the silver chloride reference electrode was placed near the inner wall of the working electrode. The auxiliary electrode (platinum or graphite) compartment situated in the centre of the cell was separated by a fine porosity fritted glass disk S5. The glassy carbon (Philips Zentrallaboratorium, GmbH, Aachen) working electrode cell is shown in Fig. 1. The electrolyzed

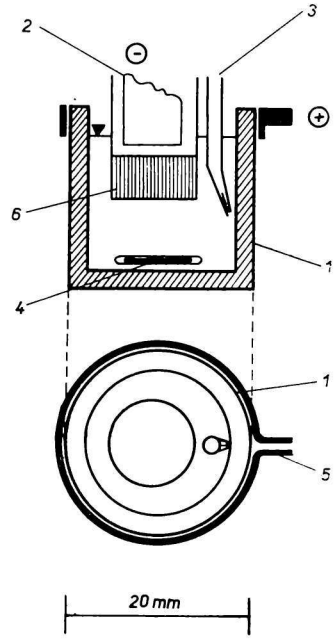

Fig. 1. Glassy carbon working electrode coulometric vessel.
1. working electrode; *2.* auxiliary electrode; *3.* reference electrode; *4.* stirring bar; *5.* lead to working electrode; *6.* fritted glass disk.

Table 1

Results of the controlled potential coulometric determination of cobalt(II)

Taken Co(II)	Found Co(II)	In the presence of				
		Ni(II)	Fe(II)	Cr(III)	Mn(II)	Zn(II)
		[μg]				
0.059	0.0589	–	–	–	–	–
0.648	0.635	–	–	–	–	–
0.825	0.604[a]	117 420	–	–	–	–
15.20	14.998[b]	–	–	–	–	–
3212	3201[b]	–	–	–	–	–
0.826	0.789	1.64	–	–	–	
1.591	1.571	3.23	–	–		–
0.059	0.0594	0.12	0.11	–	–	–
1.473	1.499	2.94	2.79	–	–	–
0.826	0.785	1.64	1.56	1.46		–
1.238	1.267	2.47	2.36	2.18	–	–
1.002	0.989	2.00	1.90	1.77	1.87	–
1.355	1.316	2.70	2.57	2.39	2.53	
0.766	0.735	1.53	1.45	1.35	1.43	1.70
1.238	1.213	2.47	2.35	2.18	2.31	2.75

a) The negative error is probably due to Fe(III) present as impurity in the great excess of nickel salt.

b) These results were obtained using the platinum working electrode cell and an electronic integrator, other values were calculated from log *i* *vs.* *t* plots and the electrolysis was carried out in the glassy carbon electrode vessel.

solution was stirred with an electromagnetic stirrer. The composition of the anolyte and catholyte was identical.

The quantity of electricity passed was determined either using an electronic integrator (included in the OH-404 set) or calculated from log i *vs.* t plots [17].

Results and discussion

From the results of the preliminary voltammetric study of pure Co(II) solutions and in the presence of Fe(II), Ni(II), Mn(II), Cr(III), and Zn(II) the working potential range from +0.40 to +0.50 V *vs.* saturated silver chloride electrode was chosen. As expected, pH changes in the 3.0—4.8 range do not affect the electrochemical oxidation potentials of the cobalt(II) complex. The influence of the background current was eliminated by the following procedure: the supporting electrolyte was first electrolyzed at the working potential until the current decreased to a negligible or practically constant value and then the aliquots of sample were added. Using the carbon working electrode lower background currents were observed.

Table 1 shows typical results of the determination of cobalt alone and in the presence of the above-mentioned ions. The slopes of the log i *vs.* t plots were about -0.009 s^{-1} in the case of the platinum working electrode cell and -0.0030 to -0.0047 s^{-1} for glassy carbon vessel.

Fig. 2 shows the variation of the electrolysis current during the determination of 0.989 μg Co(II) in the presence of a twofold molar excess of Ni(II). The supporting electrolyte was a 0.1 M acetate buffer containing 0.05 M-1,10-phenanthroline (pH 4.8). Before addition of the sample ($t = 0$) the background current was practically constant (0.6 μA). This value was subsequently subtracted from the values of the electrolysis current after addition of the cobalt sample. The logarithm of the current intensity is a linear function of time with slope -0.0047 s^{-1} and this allows the calculation of the quantity of electricity passed. The time required for homogenization of the solution and formation of the oxidizable complex after the sample addition is negligible compared with the duration of the electrolysis.

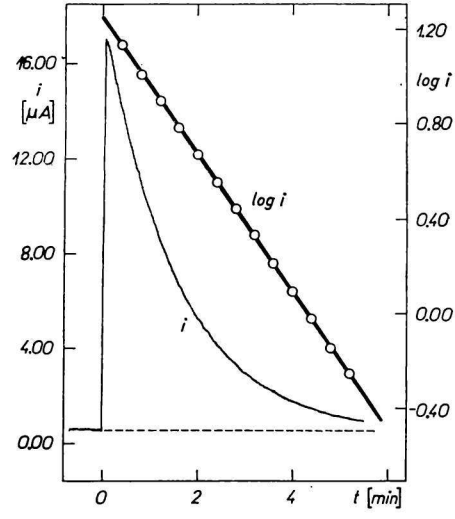

Fig. 2. Variation of current and its logarithm during electrolytic oxidation of cobalt(II) complex.

The estimate of the standard deviation for one measurement is 1.6% rel. at the 0.05 level of significance, as calculated from ten determinations of 2.0×10^{-8} g-ion Co(II).

Controlled potential oxidation of the tris(1,10-phenanthroline) cobalt(II) complex enables the precise coulometric determination of cobalt. Precision and accuracy of the determination of microamounts of cobalt are quite satisfactory and are limited mainly by sample volume measurement. The determination of the quantity of electricity passed using the log *i vs. t* plot eliminates the need for an integrator. In the presence of a sufficient excess of the complexing agent Fe(II), Ni(II), Mn(II), Cr(III), and Zn(II) can be tolerated. Fe(III) interferes with the determination.

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