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Abstract

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DIFFERENTIAL AMPEROMETRIC TITRATION OF IRIDIUM, PALLADIUM, IRON, AND COPPER WITH A SOLUTION OF 8-MERCAPTOQUINOLINE

(Presented by Academician I. V. Tananaev, 27 VI 1963)

The amperometric method makes it possible to use the successive oxidation or precipitation of several elements by one and the same reagent for their quantitative determination. According to the literature, the developed procedures for differential amperometric titration are based on the use of reactions of a single type. Thus, when two oxidants or reductants are present in solution, whose oxidation-reduction potentials differ considerably from one another, their successive determination is possible if the electrochemical behavior of the components leads to a titration curve with two equivalence points. These titrations, based on the use of oxidation-reduction reactions, are most often carried out with a change in the electrode potential upon passing from one cation being determined to another.

Table 1

Real oxidation-reduction potentials of the 8,8′-diquinolyldisulfide-8-mercaptoquinoline system (ORP)

Medium	Magnitude of measured emf, V	Potentials from data of potentiometric titration, V
1 N HCl	+0.422	+0.420
1 N H_2SO_4	+0.440	+0.445
0.2 N HCl	+0.370	+0.372
0.2 N H_2SO_4	+0.385	+0.385
pH 1	+0.312	+0.312
pH 2	+0.280	+0.280
pH 3.1	+0.235	+0.240
pH 3.8	+0.215	+0.216
pH 4.85	+0.190	+0.189
pH 5.8	+0.160	+0.160
pH 7.6	+0.085	+0.080
pH 8.5	+0.045	+0.050

Figure 1

Figure 1: Figure 1

Medium	Magnitude of measured emf, V	Potentials from data of potentiometric titration, V

I. P. Alimarin, Z. A. Gallai, and other authors have described determinations of Fe^{2+} and V^{4+} with salts of quadrivalent cerium (1), Fe^{3+} and Mo^{6+} with salts of divalent chromium (2), and Fe^{3+} and Ce^{4+} with ascorbic acid (3). On the basis of the successive precipitation of components with different solubility products, amperometric titration of Pb^{2+} and Ba^{2+} with chromate ions (4), and of Cu^{2+} and Ni^{2+} with dimethylglyoxime (5), has been proposed.

We have developed a new differential amperometric method for the determination of metals, in which both oxidation-reduction reactions and precipitation reactions are used; as a result, the combinations of cations suitable for successive titration are considerably expanded. In addition, the possibility is opened of increasing the number of elements determined in a single titration: from two to four and more.

As the titrating reagent, 8-mercaptoquinoline was used, which forms stable inner-complex salts with cations of the hydrogen sulfide and ammonium sulfide groups (6,7) and possesses some reducing properties. As our experiments have shown, 8-mercaptoquinoline is oxidized at a platinum electrode and can be successfully used in the amperometric method of analysis (8). The titration conditions of several cations (Cu, Pd, Au, Cd, In), whose determination is based on re-

reaction for the formation of thiooxinates (8–10). Iron(III) and iridium(IV) are reduced by 8-mercaptoquinoline. The resulting Fe^{2+} and Ir^{3+} are oxidized at a platinum electrode at an applied potential of $+0.9$—$+1$ V. The oxidation-reduction potentials of the system 8,8′-diquinolyldisulfide—8-mercaptoquinoline were determined. Their values in the acidity range from pH 8.5 to $1N$ acid were determined by two methods: by direct measurements of the electromotive forces of specially composed cells and by analysis of the curves of potentiometric titration of 8-mercaptoquinoline with iodine (Table 1). The product formed as a result of the reduction reaction of Ir^{3+} under the conditions of amperometric titration does not react with 8-mercaptoquinoline.

Fig. 1. Curves of amperometric titration of iron, iridium (indicator—copper) and palladium (indicator—iron).
1 —Ir^{4+}; 2 —Fe^{3+}; 3 —$Pd^{2+} + Fe^{3+}$

Fig. 2. Curves of differential amperometric titration of iridium, palladium, iron and copper with a solution of 8-mercaptoquinoline

Figure 2

Figure 2: Figure 2

quinoline. Its diffusion oxidation current is recorded in all media. For iron it is necessary to create a definite acidity ($pH < 2$), since in neutral and weakly acidic solutions a precipitate of iron thiooxinate is formed. The diffusion current on the titration curves of iridium and iron increases without limit, since the oxidation curves of the ions of the metals listed pass into the oxidation curves of the excess reagent. For indication of the equivalence point, the use of certain cations forming precipitates with 8-mercaptoquinoline was proposed. In that case the observed rise, after the reduction of Ir^{4+} and Fe^{3+}, passes into a horizontal plateau corresponding to precipitation of another metal (Fig. 1). Depending on the medium, in the amperometric determination of iridium, palladium, copper, cadmium, and zinc may be used as indicators; in the determination of iron—only copper. Palladium, which forms more stable thiooxinates than copper, is titrated before iron. The formation of inner-complex compounds decreases the concentration of the potential-determining ion, which leads to a corresponding increase in the oxidation-reduction potential of the system 8,8′-diquinolyldisulfide—8-mercaptoquinoline. It has been established that the complexing action of copper raises the potential by 0.18 V, and that of palladium by 0.42 V. Thus, at pH 1, the real oxidation-reduction potentials of the system 8,8′-diquinolyldisulfide—8-mercaptoquinoline will be, respectively, +0.492 V and +0.735 V. Comparison of the potentials Fe^{3+}/Fe^{2+}, $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ with the real potentials found for the organic reagent, taking into account that the rate of the precipitation reactions is considerably greater than the rate of the reduction reaction, confirms the possibility of the quantitative determination of iron and iridium using the listed indicators and explains the reason for the precipitation of palladium before the reduction of iron.

If copper and iron, iridium and palladium, iridium and copper, or iridium and cadmium are present in solution in comparable amounts (of the same order), their successive determination is possible. The second equivalence point is recorded owing to the appearance of the oxidation current of excess reagent. The differential amperometric determination of the listed elements is based, as noted earlier, on a combination of different types of oxidation-reduction and precipitation reactions ([11]). Comparison of the titration curves of iron and copper, iron and palladium, and palladium and iridium indicates the possibility of the successive determination of all four components. Indeed, under certain optimum conditions, various amounts of iridium, palladium, iron, and copper jointly present in solution were titrated. Good results were obtained (Table 2). The relative error does not exceed 5%.

Because of differences in the oxidation-reduction potentials of iron and iridium, the solubility products of palladium and copper thiooxynates, and the rates of the reduction and precipitation reactions, the following reactions occur successively in solution:

$$2[IrCl_6]^{2-} + 2C_9H_6NSH \rightleftarrows 2[IrCl_6]^{3-} + C_{18}H_{12}N_2S_2. \quad (1)$$

$$2[PdCl_4]^{2-} + 3C_9H_6NSH \rightleftarrows Pd_2(C_9H_6NS)_3Cl + 3H^+ + 7Cl^-. \quad (2)$$

$$2Fe^{3+} + 2C_9H_6NSH \rightleftarrows 2Fe^{2+} + C_{18}H_{12}N_2S_2. \quad (3)$$

$$Cu^{2+} + 2C_9H_6NSH \rightleftarrows Cu(C_9H_6NS)_2 + 2H^+. \quad (4)$$

Table 2

Results of the differential amperometric determination of iridium, palladium, iron, and copper with 8-mercaptoquinoline

Taken, mg	Taken, mg	Taken, mg	Taken, mg	Found, mg	Found, mg	Found, mg	Found, mg	Relative error, %	Relative error, %	Relative error, %	Relative error, %
Ir^{4+}	Pd^{2+}	Fe^{3+}	Cu^{2+}	Ir^{4+}	Pd^{2+}	Fe^{3+}	Cu^{2+}	Ir^{4+}	Pd^{2+}	Fe^{3+}	Cu^{2+}
0.333	0.3411	0.1117	0.6354	0.333	0.3387	0.1117	0.6396	0.0	−0.7	0.0	+0.6
2.001	1.0233	0.1117	0.3312	1.957	1.0403	0.1157	0.3671	−2.2	+1.7	+3.3	−3.7
1.000	0.1137	0.4463	0.1271	0.989	0.1117	0.4517	0.1271	−1.1	0.0	+1.1	0.0
1.334	0.4548	0.1675	0.0635	1.305	0.4485	0.1738	0.0635	−2.2	−1.4	+3.8	0.0
0.667	0.2274	0.3351	0.2542	0.685	0.2352	0.3278	0.2522	+2.7	+3.5	−2.2	−0.8
1.000	0.5655	0.1675	0.1271	1.003	0.5645	0.1712	0.1251	+0.8	−0.7	+2.2	−1.6
0.667	0.1137	0.5585	0.6354	0.633	0.1176	0.5524	0.6354	−5.1	+3.5	−1.1	0.0
2.668	0.6882	0.2234	0.3178	2.650	0.6765	0.2283	0.3198	−0.7	−1.7	+2.2	+0.6
0.333	0.4548	0.6702	0.3812	0.333	0.4548	0.6590	0.3954	0.0	0.0	−1.7	+3.7
1.334	0.7959	0.2234	0.5085	1.416	0.7848	0.2234	0.5169	+4.6	−1.4	0.0	+1.7
0.667	0.3411	0.6702	0.3813	0.646	0.3553	0.6624	0.3724	−3.2	+4.2	−1.1	−2.4

On the platinum microelectrode:

$$[IrCl_6]^{3-} - e \rightleftarrows [IrCl_6]^{2-}. \quad (5)$$

$$Fe^{2+} - e \rightleftarrows Fe^{3+}. \quad (6)$$

$$2C_9H_6NSH - 2e \rightleftarrows C_{18}H_{12}N_2S_2 + 2H^+. \quad (7)$$

Figure 2 gives the curves of differential amperometric titration of four components. Upon addition of the first portions of reagent, reduction of Ir^{4+} occurs (reaction 1). The Ir^{3+} ions formed are oxidized at the electrode (reaction 5) and cause an increase in the diffusion current (section a–b). After reduction of Ir^{4+}, palladium is precipitated (reaction 2). This period corresponds to the first horizontal plateau (section b–c). Then 8-mercaptoquinoline reduces iron (reaction 3), while Ir^{3+} and Fe^{2+} are oxidized at the electrode (reactions 5, 6). After all the iron has been reduced, copper is precipitated (reaction 4). A second plateau is observed on the titration curve (section d–i). The final rise of the diffusion current corresponds to the oxidation current of the excess reagent (reaction 7). In the proposed method, the elements being determined themselves (palladium, iron, and copper) also serve as amperometric indicators.

Optimal titration conditions. The test solution must have an acidity from pH 1 to 0.25 N. The presence of $Cl^- > 1$ mg/ml is obligatory. To prevent coprecipitation of copper and palladium, several milliliters of a 1% solution of the surface-active substance OP-10 are added. The concentrations of Ir, Pd, Fe, and Cu being determined must be comparable.

The titration is not interfered with by the presence of thousandfold excesses of zinc, cadmium, cobalt, nickel, and other elements that do not react with 8-mercaptoquinoline. If not all four of the elements to be determined are present in the solution, but any three of them are, introduction of the fourth makes it possible to determine accurately the content of each.

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