CATALYTIC EFFECTS IN THE POLAROGRAPHY OF INORGANIC COMPOUNDS

S. I. Sinyakova* and Yu. S. Milyavskii

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In recent years many papers have appeared on the theoretical aspects of catalytic currents (i_c). In classical and alternating-current polarography these currents are recorded on dropping mercury, flow-type, quiescent, solid, and film electrodes by chronoamperometric, chronopotentiometric, and chronocoulometric techniques [1-14]. A series of equations relating to the rate constant of the chemical stage and the electrode parameters of the process have been obtained. However, the catalytic currents, which were first described 40 years ago, have not yet found sufficiently widespread use in analytical chemistry. The reason for this is inadequate study of the mechanism of the chemical reaction which is coupled with the electrode process.

The oxidative–regenerative scheme, as a variant of the theory of compensating reactions introduced into polarography from homogeneous catalysis, has received most attention. According to this scheme, the redox characteristics of the reagents in their thermodynamical interpretation are considered during the investigation of the chemical stage. However, as shown in [15-19], this approach is insufficiently precise in the light of the modern theories of coordination chemistry.

The standard electrode potentials only indicate the probability and direction of the process, and its kinetics are completely controlled by the atomic and electronic configurations of the reagents [20-21]. Therefore, the magnitude of i_c, which is determined unambiguously by the rate of the chemical stage, depends not on the thermodynamic but on the kinetic parameters. Thus, irrespective of the difference between the standard electrode potentials of the catalyst and the substrate, the electrode process is influenced only by reactions with rate constants exceeding 10^1-10^2 liter/mole·sec [22].

In solution the metal ions are present as coordination compounds with a central atom (the metal ion) and a ligand (the components of the solution). Consequently, the reactions in which they participate obey the laws of coordination chemistry. Almost any case of electron transfer (apart from tunnelling) is preceded by substitution of one of the ligands in the coordination sphere of the reagent by a bridging group or directly by the substrate [20].

Systems in which catalysis of the polarographic reduction of depolarizers is observed can be divided into two classes, depending on the ratio of the redox and donor–acceptor characteristics in the reagents. The substitution of one ligand from the coordination sphere of the catalyst increases the liability of the remainder except in cases where it leads to a change in the order in which the t_{2g} and l_g orbitals are filled. Such substitution should always be accompanied by an increase in the rate of reactions where the central atom takes part in the kinetic stages. If the entering ligand is redox-active the rate of its transformation in the coordination sphere increases, for it is controlled by the rate at which the electronic and atomic configuration of the metal ion rearranges [23-24]. If the substituting ligand does not exhibit redox characteristics in the region of the electrochemical activity of the central atom, the effect of its introduction into the coordination sphere is completely reflected in the change in the behavior of the central atom.

Thus, if the substrate or redox-active ligand takes part in the chemical stage of the formation process, the reaction goes to some degree of completion. The depolarizer responsible for the exaltation of the current is either the final product or, which more frequently arises, one of the intermediate compounds in the reaction possessing the

* Deceased.

Vernadskii Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR. Translated from Zavodskaya Laboratoriya, Vol. 37, No. 10, pp. 1153-1158, October, 1971. Original article submitted January 5, 1971.

highest (among the other compounds) affinity towards the electrode. Catalytic currents with this type of mechanism are most widely represented among the investigated systems.

The catalytic currents recorded in systems where the substrate is a redox-active ligand differ according to the ratio of the donor–acceptor characteristics of the reagents [19]. If the d shells of the catalyst are not filled, the electrons from the electrode are taken into the atomic orbitals of the metal. Consequently, in form and position on the potential axis, i_c will be identical with i_d, since the rate of the chemical stage depends linearly on the concentration of the catalyst, and the variation in the latter repeats the form of the diffusion wave. If the catalyst is in a higher oxidation state [Mo (VI), W (VI), Nb (V), Ti (IV), etc.], the electrons are taken into the molecular orbitals of the charge-transfer complex. In this case the reduction wave of the intermediate compound will lie on the positive side of the diffusion current for the catalyst, and only the substrate is reduced in the electrode catalytic event with regeneration of the catalyst. Such behavior of the catalytic current in the presence of transition-metal ions clearly correlates with the coordination characteristics of the reagents. In the first case the substrates exhibit their π-acceptor characteristics, and in the second case they exhibit their π-donor characteristics [19].

The second class of i_c values represents the case where the entering ligand, while not reacting with the central atom in the normal chemical sense, facilitates the electrode process and labilizes the coordination sphere. This secures a more rapid rearrangement of the electronic structure of the depolarizer from the "orbital of the transition state" [24] to the electronic and atomic configurations of the final product. Here there is a shift in the half-wave potential for the reduction of the depolarizer from the region corresponding to the less liable form towards positive potentials approaching the reversible potential. Such, for example, are the catalytic currents described in [25-26].

Thus, the polarographic catalytic systems should obey the laws of nucleophilic substitutions S_N [27] either directly or indirectly through the macroscopic equation for the process. The analysis of the published and experimental data [15-19] confirms the coordination scheme for the development of i_c proposed in [16]. According to this scheme, the retarded stage of the process is the substitution of coordinated water or a ligand of equal strength at the catalyst by the substrate.

By means of an investigation into the model system Fe (III) – H_2O_2 it was possible to reach the following conclusions about the features of the mechanism for the development of i_c:

1) The catalytic current is due to the coordination characteristics of the element;

2) A catalytic current only arises in those cases where the catalyst is in a state which is labile towards substitution;

3) The process of the development of i_c passes through a stage involving the formation of an intermediate compound by the substitution of coordinated water at the catalyst by the substrate; this stage is the kinetic stage;

4) Chelation greatly enhances the catalytic characteristics of the metals in high-spin compounds, increasing the mobility of the water or other monodentate ligands in the coordination sphere and axial ligands in particular;

5) The presence of strong-field ligands in the solution completely or partially inhibits i_c.

With the coordination scheme for the process of the development of i_c it is possible to describe the majority of the known (in the literature) catalytic polarographic systems in terms of a common mechanism over a wide range of reagent concentrations. It correlates fairly well with experiment. There is no need to introduce additional reactions depending on the variation in the composition of the solution in the description of the process, as must be done in the case of the oxidative–regenerative mechanism [28-29]. Thus, the coordination approach to the description of the development of i_c is preferred from the standpoint of the chemical mechanism of the process.

The currently existing theoretical equations (Brdicha, Delahay, Koutecky, et al.), which quantitatively relate i_c to the rate constant of the chemical stage, were derived on the premise that the regeneration of the initial depolarizer is responsible for the exaltation of the current. Here the kinetics are determined by the transfer of an electron between the substrate and the catalyst. As shown in [16-19], these equations have definite limitations in respect of the range of substrate and catalyst concentrations and also reaction rates. They agree with experiment best of all under conditions where the real order of the reaction is pseudomonomolecular. Experiment is described somewhat better by a formal equation of the Langmuir type, obtained by the phenomenological analysis of catalytic polarographic systems [18]:

$$i_c = \frac{I_{max} \cdot C_S}{K_{em} + C_S}, \quad (1)$$

where I_{max} is the asymptotic value of i_c, C_S is the concentration of the substrate, and K_{em} is an empirical constant.

TABLE 1. The Rate Constants and Instability Constants of the Intermediate Compounds, Obtained from the Equation

System	$K_{i.calc}$	k_{calc}	k_{lig}	Acidity	Reference
$Fe^{+3}-H_2O_2-H_2SO_4$	0,07—0,09	58—78	23—78	0,01—0,5 m. H_2SO_4	[19,34]
Fe (III) EDTA—H_2O_2—Acetate	0,022	$1,0-1,3\cdot10^4$	$7\cdot3\cdot10^3$	pH 4,7	[28]
Cu (II)—H_2O_2—HCl	0,163	53,5	49—58,5	0,1—1-m HCl	[29]
Cr (III) EDTA—NO_3^-—Acetate	0,173	35,0	30,1—35,1	pH 4,7	[31]
Ti (IV) EDTA—H_2O_2	0,01	$1,1\cdot10^4$	$(6\pm2)\cdot10^3$	pH 2	[32]
Ti (IV) EDTA—H_2O_2	0,06	$1,2\cdot10^4$	$(6\pm2)\cdot10^3$	pH 0,9	[32]
Ti (IV)—BrO_3^-	0,03	$7,8\cdot10^4$	$(6,7\pm3)\cdot10^4$	pH 3,3	[33]
Ti (IV) NTA—H_2O_2	0,011	$2\cdot10^3$	$(2\pm1)\cdot10^3$	pH 2	[32]
Ti (IV) Sal—H_2O_2	0,018	$3\cdot10^3$	$(3\pm1)\cdot10^3$	pH 3,6	[32]

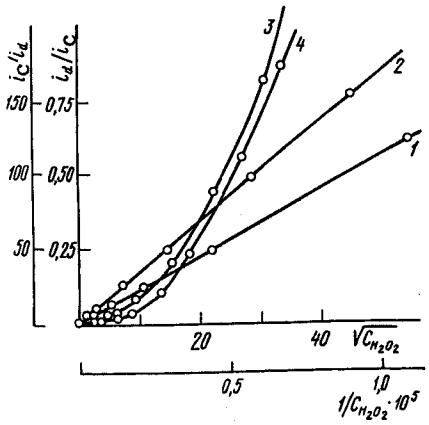

Fig. 1. The dependence of i_d/i_c on $i/C_{H_2O_2}$ (curves 1 and 2) and the dependence of i_c/i_d on $\sqrt{C_{H_2O_2}}$ (curves 3 and 4), calculated from the data in [17]: 1, 3) Fe (III) BSED catalyst; 2, 4) Fe (III) TEA catalyst.

By analogy with the Langmuir equation the expression $C_S/(K_{em} + C_S)$ can be considered to be the proportion of combined catalyst.

However, this equation only describes the experimental data but does not give a quantitative relation between the macrocharacteristics of the process and the kinetic parameters of the reaction. To obtain such a relation it is necessary to obtain a simultaneous solution of the diffusion and kinetic problems, similar to the way in which this was done within the scope of the regeneration scheme. In the case of the coordination mechanism the kinetic equation and the course of the process are more complicated than this scheme, and the use of an accurate solution by the Koutecky method gives rise to enormous difficulties.

The problem was solved by using the reaction-layer concept in analogy with [30]. The following scheme was examined:

$$A + n\bar{e} \rightarrow K; \quad K + S \rightleftarrows KS; \; KS + m\bar{e} \rightarrow K + P, \quad (2)$$

where A is the initial depolarizer, S is the substrate, K is the catalyst, KS is the intermediate compound, and P is the product from the catalytic reduction of the substrate.

Under pseudomonomolecular conditions:

$$[S] \gg [K]. \quad (3)$$

In this case the flow of the compounds at the electrode for scheme (2) can be represented in the following form:

$$D\frac{C^o_{KS}}{\mu} = \mu k \frac{C^o_K + C^e_K}{2}\cdot C^v_S, \quad (4)$$

where D is the diffusion coefficient of A, μ is the thickness of the reaction layer, and k is the rate constant of the forward reaction. The superscripts on the concentrations have the following meanings: o, the outer surface of the reaction layer; e, the electrode surface; v, the volume (initial) concentration. If the transformations employed in [30] are used, it is possible to obtain:

$$i_c = a\cdot C^v_K \frac{C^v_S}{K_i + C^v_S}\sqrt{\frac{Dk\left(2K_i + C^v_S\right)}{2}}, \quad (5)$$

where a represents the electrical constants, and K_i represents the instability constants of KS.

According to the coordination scheme [16], the diffusion coefficient of the complex KS can be taken as approximately equal to the diffusion coefficient of the initial depolarizer. Therefore, in view of the fact that $\bar{q} = 0.51\,m^{2/3}t^{2/3}$, and $\varkappa = 0.627 \cdot F \cdot n \cdot 10^{-3} D^{1/2} m^{2/3} t^{1/6}$, Eq. 5 can be presented in the following form:

$$i_c = 0.81 i_d \frac{nC_S^v}{K_i + C_S^v} \sqrt{\frac{k\left(2K_i + C_S^v\right)t}{2}}.$$

or

$$i_c/i_d = 0.81 \frac{n \cdot C_S^v}{K_i + C_S^v} \sqrt{\frac{k\left(2K_i + C_S^v\right)t}{2}}, \tag{6}$$

where n is the ratio of the number of electrons taking part in the electrode stage of the catalytic and diffusion processes.

This equation describes the catalytic currents which arise in scheme (2). Its special cases are associated with the stability ratio of the intermediate complex KS and the range of substrate concentrations, i.e., K_i and C_S^v [30]. For instance, when an unstable intermediate complex is formed or when the concentration of the substrate is low, i.e., when $K_i \gg C_S^v$, Eq. (6) converts to the following form:

$$i_c/i_d = 0.81 n C_S^v \sqrt{kt/K}, \tag{7}$$

i.e., is analogous with the Brdicka equation in the nature of the $i_c - C_S^v$ relationship. When a stable complex is formed or when the concentration of the substrate is high, i.e., when $K_i \ll C_S^v$, Eq. (6) takes the following form:

$$i_c/i_d = 0.81 n \sqrt{kC_S^v t/2}. \tag{8}$$

Equation (8) almost coincides with the asymptotic equation of Koutecky. Thus, for the $Fe^{3+} - H_2O_2$ system, where n = 2 [16], it takes the following form: $i_c/i_d = 0.81\sqrt{2ktC_{H_2O_2}}$.

Thus, Eq. (6) can be considered to be a general case of the expression for i_c, relating it to the parameters and kinetics of the process.

Equation (6) is not suitable for practical use in the general form, for its use requires a knowledge of the value of one of the constants K_i or k for the determination of the other from the experimental data. When these data are not available, Eq. (6) is suitable only for a qualitative description of the systems. To reduce it to a form which is suitable for use Eq. (6) is converted into the following form by expansion of the factor under the square-root sign into a power series:

$$i_c/i_d = 0.81 n \frac{C_S^v}{K_n + C_S^v} \sqrt{kK_i}\, t. \tag{9}$$

Here, the error arising from the neglect of terms of second or higher powers in C_S^v (in the case where $C_S^v \leq 0.5 K_i$) amounts to <10%.

Equation (9) is solved graphically by the method of double reciprocal quantities. For this purpose it is written in the following form:

$$i_d/i_c = \frac{1.23\sqrt{K_i}}{n\sqrt{kt}} \cdot 1/C_S^v + \frac{1.23}{n\sqrt{K_i kt}}. \tag{10}$$

By plotting a curve for the dependence of i_d/i_c on $1/C_S^v$, it is possible to obtain a straight line with a gradien of $1.23\,K_i^{\frac{1}{2}}/n(kt)^{\frac{1}{2}}$. The intercept on the ordinate axis is equal to $1.23/n(K_i kt)^{\frac{1}{2}}$, and the intercept on the extensio of the abscissa axis is equal to $1/K_i$ (i.e., K_{st}). By determining the slope of the straight line and the intercepts graphically it is possible to calculate K_i and k from the following equation:

$$K_i = A/B, \tag{11}$$

where A is the tangent of the slope of the straight line, and B is the intercept on the ordinate axis.

The value obtained for K_i can be checked by means of the expression:

$$K_i = -1/C, \tag{12}$$

where C is the intercept on the extension of the abscissa axis.

The rate constant of the chemical stage is determined from the equation:

$$k = \left(\frac{1.23}{n}\right)^2 \cdot \frac{1}{A \cdot B \cdot t} . \qquad (13)$$

Equation (9) also confirms the accuracy of the empirical expression (1) and makes it possible to interpret the meaning of the constant K_{em}. In fact, for a constant catalyst concentration (i_d = const) and by combining all terms in Eq. (9) which are independent of C_S^v, it is possible to obtain the following equation:

$$i_c = \frac{R \cdot C_S^v}{K_i + C_S^v} . \qquad (14)$$

Comparison of Eqs. (1) and (14) shows that they are identical. Consequently, I_{max} from Eq. (1) is identical with R from Eq. (14) and K_{em} from Eq. (1) can be considered to be equal to K_i from Eq. (14).

By making use of the properties of equations with the hyperbolic form of type (1) and (14) it is possible to make a preliminary assessment of K_i directly from the relationship between i_c and C_S^v.

From Eqs. (1) and (14) it follows that K_i (K_{em}) = C_S^v for $i_c = I_{max}/2$ (or R/2). Thus, the K_i (or K_{em}) value is equal to the concentration of the substrate at which the catalytic current is equal to half its asymptotic value. In the case of systems where the $i_c - C_S^v$ relationship rapidly reaches saturation, the determination of K_i (or K_{em}) from the experimental curve can be carried out fairly accurately. This is particularly important for the determination of the ratio of C_S^v and K_i, i.e., for the region where Eqs. (6) and (9) are applicable. Equation (9) was checked for the $Fe^{3+} + H_2O_2$ system and certain other systems where the authors give the necessary data.

As seen from Table 1, the values for the rate constants of the chemical stage, determined from Eq. (9), are in agreement with the generally accepted values.

The relationships between i_c/i_d and $C^{\frac{1}{2}}_{H_2O_2}$ (according to Koutecky) and between i_d/i_c and $1/C_{H_2O_2}$ [Eq. (10)] are given in Fig. 1. The experimental points fit well on to the lines 1 and 2. At the same time they deviate appreciably from the linearity predicted by the asymptotic equation of Koutecky for the relationship between i_c/i_d and $C^{\frac{1}{2}}_{H_2O_2}$, although the conditions for its use are satisfied [17].

The lines for i_d/i_c against $1/C_{H_2O_2}$ pass through the origin of the coordinates, and k and K_i cannot therefore be determined separately in this case. Their ratios [$5 \cdot 10^9$ for Fe (III) BSED* $- H_2O_2$ and $1.6 \cdot 10^9$ for Fe (III) TEA† H_2O_2] were calculated from the gradient.

The nature of the relation between i_d/i_c and $1/C_{H_2O_2}$ shows that Eq. (7) does in fact hold over the whole range of H_2O_2 concentrations (10^{-6}-10^{-2} M) investigated in [17]. In the systems examined the stability of the intermediate compounds is almost the same as in acidic solution since, according to the condition for the use of Eq. (7), $K_i \gg C_S^v$, and consequently $K_i \geq 10^{-2}$ M.

Thus, Eq. (6), derived from the coordination premises, correlates with experiment for systems which differ in nature and covers a wider range of substrate concentrations than the Koutecky equation.

Catalytic phenomena of a coordination nature have also been observed in the method of amalgam polarography with accumulation. Apart from the previously described catalytic reduction of hydrogen peroxide during the anodic dissolution of copper and lead [35], the formation of a current for the dissolution of cobalt accumulated on a stationary mercury electrode in the presence of increasing quantities of Cl^-, CNS^-, and Pyr has also been described.

As shown in [36], the dependence of the dissolution current on the concentration of the ligand is extremal in ature. The ligand concentrations corresponding to the peaks on the curves for various cobalt concentrations behave s the square roots of the ratio of the metal concentrations. From this it was concluded that a greater degree of lailization of the coordination sphere of Co^{2+} than that secured by its equation is required for the electrode process o go to completion and for the corresponding rearrangement of the electronic and atomic configurations of cobalt in Co^{2+}. Such labilization is achieved by the introduction of two ligands with a greater donor ability than that of

* BSED is bissalicylalethylenediimine.
†TEA is triethanolamine.

water into the coordination sphere of Co^{2+}. Therefore the kinetics of the anodic dissolution of the accumulated cobalt are controlled by the formation of a complex of the $[CoL_2(H_2O)_4]^\circ$ type in the case where L = Cl^-, CNS^- or of the $[CoL_2(H_2O)_4]^{2+}$ type where L = Pyr, NH_3, etc.

The coordination approach to the problem of the development of i_c makes it possible to forecast the catalytic polarographic characteristics and to make a guided selection of systems for analytical purposes on the basis of data on the structure and the proportions of the donor and acceptor characteristics of the reagents [37].

For analytical work the coordination scheme suggests the following recommendations for the selection of pairs of reagents with regard to the rules given by Toropova and Zabbarova [40].

The substrate and the composition of the solution should be chosen so as to ensure the maximum lability of the determined metal in the compound where it will act as catalyst. For the majority of transition metals these are nitrogen- and oxygen-containing chelates with the donor groups in the equatorial plane of the octahedron and two monodentate ligands in the 5-6 positions. (It is these ligands which are readily substituted by the substrate.)

It is necessary to ensure the maximum affinity of the substrate towards the catalyst. Thus, the most suitable substrates for catalysts in the higher valence state are hydrogen peroxide and its various derivatives. In this case hydrogen peroxide exhibits its π-donor ability. Here the waves are shifted to the strongly positive region. In the case of catalysts with filled d levels, where the substrate exhibits its π-acceptor activity, hydrogen peroxide, hydroxylamine, and the nitrate, perchlorate, and chlorate anions and their derivatives can be employed as substrates. The catalytic wave will coincide in potential with the diffusion wave of the catalyst. In this case the choice of substrate is dictated by the ratio φ^0 of the reagents and the reaction rate.

By means of these ideas it has been possible to develop highly sensitive and selective methods for the determination of iron [37], titanium [38], and niobium [39] in high-purity compounds, with sensitivities of $n \cdot 10^{-9}$ g/ml for iron and titanium and 10^{-8} g/ml for niobium with a variation coefficient not greater than 10%.

LITERATURE CITED

1. J. Heyrovsky and J. Kuta, Principles of Polarography [Russian translation], Izd. Mir (1965).
2. O. Fischer and O. Dracka, Coll. Czech. Chem. Comm., 24, 3046 (1959).
3. J. Weber, Coll. Czech. Chem. Comm., 24, 1770 (1959).
4. S. Feldberg, J. Phys. Chem., 73, 1238 (1969).
5. M. Mastragostino, L. Nadjo, and J. M. Saveant, Electrochem. Acta, 13, 721 (1968).
6. P. Delahay, C. C. Mattax, and T. J. Berzins, J. Am. Chem. Soc., 76, 5319 (1954).
7. J. W. Ashley and C. N. Reilley, J. Electroanal. Chem., 7, 253 (1964).
8. K. N. Klatt and W. J. Blaedel, Anal. Chem., 40, 512 (1968).
9. T. G. McCord and D. E. Smith, Anal. Chem., 41, 116 (1969).
10. H. L. Hung, J. R. Delmastro, and D. E. Smith, J. Electoanal. Chem., 7, 1 (1964).
11. O. Fischer, O. Dracka, and E. Flscherova, Coll. Czech. Chem. Comm., 26, 1505 (1961).
12. T. G. McCord and D. E. Smith, Anal. Chem., 40, 1959, 1967 (1968).
13. M. L. Olmstead and R. S. Nicholson, Anal. Chem., 41, 862 (1969).
14. T. G. McCord and D. E. Smith, J. Electroanal. Chem., 26, 61 (1970).
15. S. I. Sinyakova and Yu. S. Milyavskii, Zh. Neorgan. Khim., 12, 633 (1967).
16. Yu. S. Milyavskii and S. I. Sinyakova, Izv. Akad. Nauk SSSR, Ser. Khim., 2384 (1967).
17. Yu. S. Milyavskii and S. I. Sinyakova, Izv. Akad. Nauk SSSR, Ser. Khim., 988 (1968).
18. Yu. S. Milyavskii and S. I. Sinyakova, Legkie Splavy, 92 (1969).
19. Yu. S. Milyavskii, Candidate's Thesis [in Russian], GEOKhI, Moscow (1967).
20. J. Halpern, Quart. Rev., 15, 207 (1961).
21. L. D. Maeyer and K. Kustin, Ann. Rev. Phys. Chem., 14, 5 (1963).
22. A. A. Vlcek, VIII Int. Conf. Coord. Chem. Austria Plenary Lectures (1964).
23. A. A. Vlcek, Rev. Chim. Miner., 5, 299 (1968).
24. A. A. Vlcek, Progress in Polarography, Int. Publishers, Vol. 1 (1962), p. 269.
25. Ya. I. Tur'yan et al., Élektrokhimiya, 2, 1185 (1966); Élektrokhimiya, 4, 1466 (1968); Élektrokhimiya, 5, 103 (1969).
26. E. Itabashi and Sh. Ikeda, J. Electroanal. Chem., 26, 103 (1970).
27. P. Ashmore, Catalysis and Inhibition of Chemical Reactions [Russian translation], Izd. Mir (1970), p. 1966.
28. B. Matyska and D. Duskova, Coll. Czech. Chem. Comm., 22, 1747 (1957).

29. I. M. Kolthoff and R. Woods, J. Electroanal. Chem., 12, 385 (1966).
30. Ya. I. Tur'yan, Élektrokhimiya, 5, 1240 (1969).
31. N. Tanaka and T. Ito, Byull. Chem. Soc. Japan, 39, 1043 (1966).
32. V. F. Toropova and R. S. Zabbarova, Izv. Vuzov, Khimiya i Khimicheskaya Tekhnologiya, 12, 1487 (1969).
33. V. F. Toropova and R. S. Zabbarova, Zh. Analiticheskoi Khim., 25, 1059 (1970).
34. I. M. Kolthoff and E. Parry, J. Am. Chem. Soc., 73, 3718 (1951).
35. S. I. Sinyakova, I. V. Markova, and N. G. Galfyan, Methods for the Concentration of Compounds in Analytical Chemistry [in Russian], Izd. Nauka (1965), p. 64.
36. I. V. Markova and S. I. Sinyakova, Zh. Analiticheskoi Khim., 26, No. 5 (1971).
37. Yu. S. Milyavskii and S. I. Sinyakova, Zh. Analiticheskoi Khim., 23, 1183 (1968).
38. G. S. Supin, in: Methods for the Analysis of Chemical Reagents and Products [in Russian], Vol. 13 (1966), p. 132.
39. S. I. Sinyakova and I. K. Stepanova, Zh. Analiticheskoi Khim., 23, 1045 (1968).
40. R. S. Zabbarova, Author's Abstract of Candidate's Thesis [in Russian], Kazan' (1970).