Polarographic Behavior of 4-Morpholine Carbodithioate and Its Use in the Amperometric Determination of Metal Ions

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Polarographic behavior of 4-morpholine carbodithioate has been studied in various base electrolytes. It gives a well defined, diffusion controlled, reversible with one electron change, anodic wave above pH 9 extending over a fairly wide span of potential, +0.2 V to −0.3 V *vs.* SCE. The relation between diffusion current and concentration is linear upto 2.7 mM (1 M=1 mol dm^{-3}) of the reagent. The reagent has been successfully applied for the amperometric determination of Bi^{3+}, Cu^{2+}, Ni^{2+}, Te^{4+}, and Zn^{2+} individually as well as in mixtures like Cu–Zn and Cu–Ni. Conditions have also been developed for the determination of copper, nickel, and zinc in various alloys. The error does not exceed more than ±0.85% in any case. The method is simple, less time consuming and easily adoptable for the micro determination of these metal ions.

4-Morpholine carbodithioates of many metals were prepared and characterized by Brown[1] and Marcotrigiano and coworkers.[2] Zinc complex has been used as a releasing agent in atomic absorption spectrometry of noble metals.[3] Beyer and Ott utilized this compound in the spectrophotometric determination of some metal ions.[4] Recently potassium salt of this reagent has been used in the gravimetric determination of tellurium, copper, bismuth, zinc, cadmium, and mercury.[5–8] Some of the metal ions have also been characterized by thin layer[9] and paper chromatography[10] using this reagent. Extraction behavior of some divalent metals with this reagent have also been studied.[11] In the present paper, the polarographic study of 4-morpholine carbodithioate in various supporting electrolytes has been undertaken with a view to explore the possibility of utilizing it as an analytical reagent for the amperometric determination of various metal ions.

Experimental

Reagents. Sodium 4-morpholine carbodithioate was prepared by the method reported by Marcotrigiano.[2] Stock solution of sodium 4-morpholine carbodithioate was prepared by dissolving a calculated amount in distilled water and standardized against a standard solution of mercury(II) nitrate using diphenyl carbazone as the indicator. The base electrolytes, potassium nitrate, potassium chloride, sodium perchlorate, ammonium tartrate, tetraethylammonium bromide, and buffers like Britton-Robinson, Michaelisborate and ammonia–ammonium chloride were prepared in distilled water from their G. R. samples. Stock solutions of various metal ions were prepared from their G.R. samples and standardized by known methods.[12]

Equipment. Polarograms in all the cases were recorded at 25±0.5 °C with a manual Toshniwal polarograph. An H-type cell with fine porosite sintered glass disk between the two compartments was used. A saturated calomel electrode used as a reference electrode was connected to one compartment of the polarographic cell through potassium chloride-agar bridge. Dropping mercury electrode had the following characteristics, m=2.08 mg/s, t=3.10 s, and H=50 cm in aqueous solution of the base electrolyte with open circuit. In all instances, the solution was deaerated with nitrogen before recording the polarogram. An ECIL digital pH meter with glass electrode was used.

Results and Discussion

Effect of pH on the Polarogram of 4-Morpholine Carbodithioate. Polarograms for 1.25 mM carbodithioate in 0.1 M ammonium tartrate +0.1 M potassium nitrate were recorded at different pH values in the range of 5.75—11.7 using Britton-Robinson buffer. An anodic wave associated with a small prewave at more negative potentials was obtained at all pH values below 9. At pH above 9.0, the prewave was almost disappeared (Fig. 1). Even though the nature of the wave remained unaffected, the values of $E_{1/2}$ shifted towards more negative potentials with

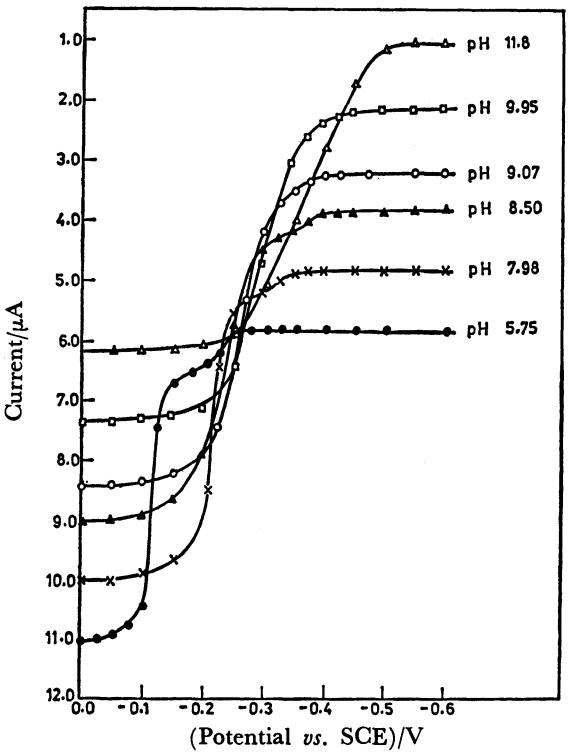

Fig. 1. Effect of pH on the polarograms of 4-morpholine carbodithioate.
4-Morpholine carbodithioate taken=1.25 mM, base electrolyte=0.1 M ammonium tartrate +0.1 M potassium nitrate, m=2.08 mg/s, drop time=3.10 s.

TABLE 1. EFFECT OF pH ON THE HALFWAVE POTENTIAL OF SODIUM 4-MORPHOLINE CARBODITHIOATE

Sodium 4-morpholine carbodithioate = 1.25 mM.
Base electrolyte = 0.1 M ammonium tartrate + 0.1 M potassium nitrate.
m = 2.08 mg/s, t = 3.10 s.

pH	$E_{1/2}$ *vs.* SCE / V	Remarks
5.75	−0.115	Pre-wave appeared
6.18	−0.135	Pre-wave appeared
6.52	−0.150	Pre-wave appeared
7.02	−0.175	Pre-wave appeared
7.51	−0.195	Pre-wave appeared
7.98	−0.215	Pre-wave appeared
8.52	−0.235	Pre-wave appeared
9.07	−0.260	Pre-wave disappeared Well define single wave obtained
9.58	−0.285	Pre-wave disappeared Well define single wave obtained
9.93	−0.300	Pre-wave disappeared Well define single wave obtained
11.26	−0.355	Pre-wave disappeared Well define single wave obtained
11.68	−0.375	Pre-wave disappeared Well define single wave obtained

increase in pH (Fig. 1, Table 1).

Polarograms of 1.25 mM of the reagent solution recorded in different buffers such as Britton-Robinson, Michaelisborate, NH_3–NH_4Cl showed that the nature of the wave was not affected by the constituents of buffers.

Effect of Various Supporting Electrolytes and Solvents. Polarograms of 1.25 mM carbodithioate at pH 9.58 in presence of 0.1 M several supporting electrolytes and solvents were recorded. The nature of the wave remained unchanged and the diffusion current constant was found to increase in the following order:

$(C_2H_5)_4NBr > KNO_3 > KCl > NaClO_4$ and

Acetonitrile > Methanol > Ethanol > DMSO > 2-Propanol.

This may be due to the variation in viscosity of the solution,[13] ($I \propto 1/\text{viscosity}$).

Effect of Mercury Pressure. Polarograms for 1.45 mM of the carbodithioate solution at various heights of the mercury column were recorded. The linear dependence of the limiting current on the square root of the height of the mercury column indicates that the rate of oxidation of 4-morpholine carbodithioate is diffusion controlled.

Effect of 4-Morpholine Carboditioate Concentration. Several polarograms with varying concentration of the reagent were recorded in 0.1 M ammonium tartrate +0.1 M potassium nitrate+ammonia buffer of pH 9.6. The anodic wave extends over a fairly wide span of potential (0.2 V to −0.3 V *vs.* SCE). The plot of diffusion current *vs.* concentration gave a straight line upto 2.7 mM of the reagent. The mean value of diffusion current constant determined with the Ilkovic equation, $I = i_d/cm^{2/3}t^{1/6}$ was found to be 1.64, which indicates the method may be applied

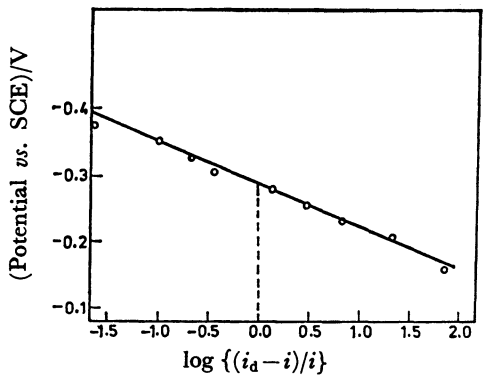

Fig. 2. Plot of $\log\{(i_d-i)/i\}$ *vs.* $E_{d.e.}$ for 2.7 mM sodium 4-morpholine carbodithioate in 0.1 M tartrate buffer (pH 11.7). Rest of the conditions are the same as in Fig. 1.

for the quantitative determination of 4-morpholine carbodithioate.

The electrooxidation of the reagent may not involve the formation of disulfide, RSSR (R=4-morpholine–thiocarbonyl) because the plots of $\log\{(i_d-i)/i\}$ *vs.* E did not yield a straight line with a slope 0.059 V/2, but yield a straight line with a slope of 0.065 V (Fig. 2) for one electron transfer. Also from Lingane equation, 1.5 $n=I$, the value of "n" corresponds to 1 to allow the conclusion that:

$$RSH + Hg \rightleftharpoons RSHg + H^+ + e \quad (1)$$

may represent the electrode reaction. Furthermore, the $E_{1/2}$ values were found to be independent of [RSH] which is characteristics of Eq. 1.

In the amperometric procedures reported for the determination of zinc,[14–15] copper,[16–17] nickel,[18] bismuth,[19] and tellurium,[20–21] the titrations have been carried out at a potential corresponding to the reduction wave of the cation concerned. It may be pointed out that an electroactive organic compound which is capable of forming an insoluble precipitate with these cations may serve as a potential titrant in their estimation. In this connection, the use of 4-morpholine carbodithioate as an analytical reagent for the quantitative estimation of bismuth, copper, nickel, tellurium(IV), and zinc has been investigated. Preliminary observations showed that under regulated conditions of base electrolyte concentration and pH, the reagent reacted with these cations to give characteristic precipitates. These observations paved the way to the estimation of microquantities of these cations by the amperometric titration procedure. The appropriate operative conditions for the quantitative estimation were established by trial experiments and are summarised in Table 2.

The applied potential (−0.2 V for Zn^{2+} and Ni^{2+}, −0.05 V for Bi^{3+}; and Te^{4+}; −0.01 V for Cu^{2+}, *vs.* SCE) was such that the metal ion was not reduced but the reagent was oxidized at the DME. The titration, therefore, involved the measurement of the anodic current of the excess titrant only after complete precipitation. Reverse L shaped curves were obtained by plotting these readings against the volume of the titrant and the end point was located graphically (Fig. 3).

Table 2. Optimum conditions for the amperometric titration of metal ions

Metal	Potential of DME *vs.* SCE / V	Supporting electrolytes	pH
Bismuth	−0.05	0.1 M Potassium nitrate 0.1 M Sodium acetate	4.5— 6.5
Copper	−0.01	0.05 M Ammonium tartrate 0.1 M Potassium nitrate	6.2—10.2
Nickel	−0.20	0.05 M Ammonium chloride 0.05 M Ammonium nitrate	7.0— 8.5
Tellurium(IV)	−0.05	0.1 M Sodium acetate acetic acid	5.0— 6.4
Zinc	−0.20	0.1 M Ammonium acetate 0.1 M Potassium nitrate	5.0— 6.4

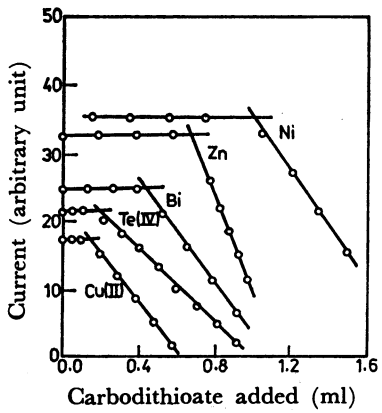

Fig. 3. Typical amperometric titration curves of bismuth, copper, nickel, tellurium(IV), and zinc. Bismuth(M/600): 2.00 ml+0.1 M sodium acetate+acetic acid (pH : 5.8). Applied potential −0.05 V *vs.* SCE. Carbodithioate: 2×10^{-2} M. Copper (1.0×10^{-3} M): 1.50 ml+0.05 M ammonium tartrate +0.1 M potassium nitrate (pH: 8.7). Applied potential: −0.01 V *vs.* SCE. Carbodithioate: 2×10^{-2} M. Nickel (1.0×10^{-3} M): 5.00 ml+0.05 M ammonium chloride+0.05 M ammonium nitrate (pH: 8.0). Applied potential −0.2 V *vs.* SCE. Carbodithioate: 0.01 M. Tellurium(IV) (2.0×10^{-3} M): 0.95 ml+0.1 M sodium acetate+acetic acid (pH: 5.7). Applied potential −0.05 V *vs.* SCE. Carbodithioate: 4×10^{-2} M. Zinc (1.0×10^{-3} M): 3.75 ml+0.1 M ammonium acetate+0.1 M potassium nitrate (pH: 6.4). Applied potential: −0.2 V *vs.* SCE. Carbodithioate: 0.01 M.

Table 3. Amperometric determination of metal ions with 4-morpholine carbodithioate

Conditions same as in Fig. 3.

Cation	Amount taken / mg	Amount found / mg	Error / %
Bismuth	0.348	0.348	0.00
	0.696	0.693	−0.43
	1.393	1.389	−0.28
	1.672	1.675	+0.18
	2.089	2.098	+0.43
Copper	0.095	0.095	0.00
	2.254	0.253	−0.39
	0.635	0.633	−0.31
	0.826	0.829	+0.36
	1.016	1.013	−0.29
Nickel	0.088	0.088	0.00
	0.176	0.175	−0.56
	0.294	0.295	+0.34
	0.352	0.350	−0.56
	0.440	0.438	−0.45
Tellurium(IV)	0.242	0.243	+0.41
	0.497	0.495	−0.40
	0.765	0.769	+0.52
	1.301	1.296	−0.38
	1.607	1.600	−0.43
Zinc	0.098	0.098	0.00
	0.176	0.177	+0.56
	0.359	0.358	−0.28
	0.490	0.492	+0.42
	0.555	0.553	−0.36

In a series of experiments an aliquot of the unknown solution of the cation was taken in the cell containing appropriate base electrolyte. The pH of the medium was adjusted to the desired value (Table 2). The solution was thoroughly deaerated by a slow stream of nitrogen gas. Necessary connections were made and the desired potential was applied to the dropping mercury electrode. A 2 ml microburette was used to deliver the titrant in small increment. In each case, the solution was stirred with nitrogen and the precipitate was allowed to stand for 1—2 min before observing the current reading. The mean deflection of the galvanometer was noted in each case. In all these determinations the solution taken in the burette was kept 20 times stronger than the solution in the cell in order to eliminate dilution effect. The end point was located graphically as the point of intersection of two straight lines (Fig. 3). The results are presented in Table 3, indicate that the microquanties of these cations can be estimated accurately.

Interferences. Metal ions such as Mo(VI), W-(VI), Te(VI), V(V), Th(IV), U(VI), Zr(IV), As-(III), Sb(III), Mg(II), Ca(II), Sr(II), Ba(II), In-(III), upto 10 fold excess; Cr(III), Al(III), and Fe-(III) upto 4-fold excess (they are precipitated as their hydroxide before titration) and Se(IV) in equal quantities can be tolerated in all cases. The interference of Pb(II), Tl(I), and Ag(I) was eliminated with sulfate and chloride ions before the titration. The interference of Cd(II), Ni(II), Hg(II), Co(II), and Zn(II) was eliminated in the determination of Te(IV), and Bi(III) by masking them with cyanide ions[22] (5 ml of 5% solution of sodium cyanide). Te-(IV) only interfered in the determination of bismuth.

In the determination of copper, Cd(II), Ni(II), Co(II), and Bi(III) interfered but the interference of Ni(II) and Co(II) can be eliminated by their successive determinations. Only Zn(II), Cd(II), and Bi(III) interfered in the analysis of nickel. Cd(II), Ni(II), Co(II), Bi(III), and Cu(II) interfered in the determination of zinc. The interference of copper can be eliminated by their successive determination. Obviously these methods are sufficiently selective and may be applied for the determination of these metal ions in complex materials. The method is quite simple rapid and easily adoptable.

It is obvious from the above results (Table 2) that some metals react with this reagent in alkaline medium while other do not. It is thus possible to titrate one metal of a mixture at higher pH and then by changing the pH after the end point to continue the titration of the other metal. This was demonstrated with a mixture of copper–zinc and copper–nickel.

Two methods have been used for the amperometric titrations. The first utilizes the decrease in height of the reduction wave of the uncomplexed copper ion during the course of titration. The second is based on the measurement of the anodic diffusion current of the excess titrating agent after the end point (Fig. 4). A combination of these two methods makes possible the determination of mixture of these metal ions.

Simultaneous Determination of Cu–Zn and Cu–Ni. To an aliquot of the synthetic mixture containing copper+zinc or copper+nickel, added 0.1 M potassium nitrate +0.01% gelatin and aqueous ammonia (pH 9.8) for the first and 0.05 M ammonium acetate +0.05 M potassium nitrate+0.01% gelatin for the second mixture. The total volume was made 20 ml in each case. The residual current of the air free solutions was noted at −0.2 V *vs.* SCE. Under these conditions only copper reacts. The titration was carried out with the reagent solution. In each case, the solution was stirred with nitrogen gas before recording the galvanometer reading. After the copper end point the pH was lowered to ≈6.5 for zinc and 7.2 for nickel by adding 1 M acetic acid at the same potential and determined the mixture end point as the intersection between residual and excess reagent lines. A series of experiments with mixture containing copper+zinc or copper+nickel in different ratios were performed. The results are given in Tables 4 and 5 respectively.

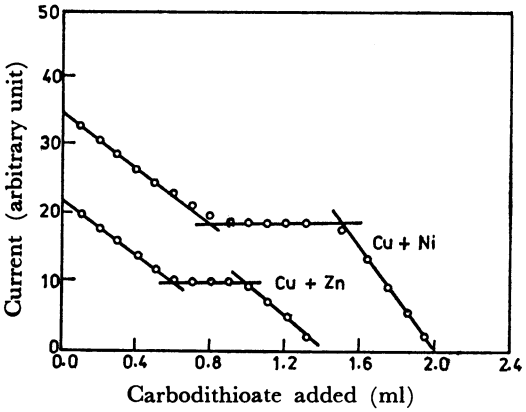

Fig. 4. Typical amperometric titration curves of Cu+Zn and Cu+Ni.
Cu+Zn: Cu(1.0×10^{-3} M): 3.00 ml+Zn(1.0×10^{-3} M): 2.00 ml+0.1 M potassium nitrate +0.01% gelatin+ammonia, pH 9.8 upto copper end point; 0.1 M potassium nitrate +0.01% gelatin+ammonium acetate, pH: 6.4 after copper end point. Applied potential: −0.2 V *vs.* SCE. Carbodithioate: 0.01 M. Cu+Ni: Cu(2.0×10^{-3} M): 4.00 ml+Ni(2.0×10^{-3} M): 3.5 ml+0.05 M ammonium chloride+0.05 M ammonium nitrate, +0.01% gelatin pH 9.5 upto copper, pH 7.2 after copper, end point. Applied potential: −0.2 V *vs.* SCE. Carbodithioate: 2×10^{-2} M.

Analysis of Alloys. 0.1 g of the alloy was taken in a beaker to which were added 10 ml of concentrated hydrochloric acid and a few ml of concentrated nitric acid. This was heated on a hot plate till the mixture dissolved completely and the solution was reduced to about 5 ml. The solution was cooled, added 5 ml of concentrated hydrochloric acid, then diluted and the final volume was made 100 ml exact

Table 4. Simultaneous determination of copper and zinc

Supporting electrolyte=0.1 M potassium nitrate+0.01% gelatin+ammonia, pH 9.8 upto copper end point; 0.1 M potassium nitrate+0.01% gelatin+ammonium acetate; pH 6.4 after copper end point.
Sodium 4-morpholine carbodithioate=0.01 M.
Applied potential=−0.2 V.

Amount taken mg		Amount found mg		Error/%	
Copper	Zinc	Copper	Zinc	Copper	Zinc
0.254	0.098	0.255	0.098	+0.39	0.00
0.222	0.164	0.222	0.165	0.00	+0.64
0.190	0.130	0.191	0.129	+0.52	−0.76
0.159	0.196	0.160	0.197	+0.60	+0.51
0.127	0.262	0.127	0.261	0.00	−0.38
0.095	0.228	0.095	0.227	0.00	−0.43

Table 5. Simultaneous determination of copper and nickel

Supporting electrolyte=0.05 M ammonium chloride+0.05 M ammonium nitrate, ammonia pH 9.5 upto copper end point, pH 7.2 after copper end point.
Sodium 4-morpholine carbodithioate=2×10^{-2} M.
Applied potential=−0.2 V.

Amount taken mg		Amount found mg		Error/%	
Copper	Nickel	Copper	Nickel	Copper	Nickel
0.127	0.734	0.127	0.731	0.000	−0.40
0.317	0.528	0.318	0.530	+0.31	+0.37
0.501	0.411	0.503	0.409	+0.39	−0.48
0.698	0.294	0.695	0.294	−0.43	0.00
0.952	0.117	0.957	0.116	+0.52	−0.85

Table 6. Determination of metals in alloys

Alloy	Composition/% Certified	Found (Average)	Error/%
Mallory No. 3	Cu:99.2 Cr:0.8	Cu:99.0	−0.20
Inconel 600	Ni:74.20, C:0.15, Mn:1.00, Fe:8.10, S:0.50, Cu:0.50 Cr:15.50, Si:0.05	Ni:74.60	+0.54
Brass No. 41.2	Cu:58.20 Zn:39.00, Pb:2.58, Fe:0.09; Sn:0.13	Cu:58.40 Zn:39.20	+0.34 +0.51
Monel wire	Cu:31.10, Ni:66.20 Fe:1.18, Mn:1.08 Mg:0.093, Al:0.93 Si:0.083, C:0.083 S:0.0037	Cu:31.00 Ni:66.60	−0.32 +0.60

in a measuring flask. The results for the determination of copper in Mallory No. 3, Nickel in Inconel-600 and the simultaneous determination of copper+zinc in Brass No. 41.2, copper+nickel in Monel wire are presented in Table 6.

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References

1) D. H. Brown, G. Aravamudan, and D. Venkappayya, *J. Chem. Soc., A*, **17**, 2744 (1971).
2) G. Marcotrigiano, G. C. Pellacani, C. Preti, and G. Tosi, *Bull. Chem. Soc. Jpn.*, **48**, 1018 (1975).
3) D. J. Nicolas and E. A. Jones, *Natl. Inst. Metall. Repub. S. Afr. Rep.* **1825** (1976); *Chem. Abstr.*, **86**, 149963z (1977).
4) W. Beyer and R. D. Ott, *Mikrochim. Inchnoanal. Acta*, 1130 (1965).
5) N. Singh, R. Kumar, and R. C. Agrawal, *Curr. Sci.*, **46**, 851 (1977).
6) N. Singh, R. Kumar, and B. D. Kansal, *J. Indian Chem. Soc.*, **55**, 240 (1978).
7) N. Singh, R. C. Agarwal, V. K. Maheshwari, and R. Kumar, *J. Indian Chem. Soc.*, **55**, 961 (1978).
8) N. Singh, S. K. Kulshreshta, A. K. Agarwal, and T. N. Srivastava, *Curr. Sci.*, **48**, 204 (1979).
9) N. Singh, R. Kumar, and B. D. Kansal, *Chromatographia*, **11**, 408 (1978).
10) R. Kumar and N. Singh, *Curr. Sci.*, **47**, 422 (1978).
11) V. S. Sastri, K. I. Aspila, and C. K. Chakorabarti, *Can. J. Chem.*, **47**, 2320 (1969).
12) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," Longmans, Green & Co., London (1964).
13) N. A. Lange, "Handbook of Chemistry," McGraw-Hill, New York (1966).
14) G. S. Deshmukh and V. S. S. Rao, *Chem. Ind. (London)*, **42**, 1434 (1968).
15) A. I. Petukhova and V. F. Toropova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **17**, 1253 (1974); *Chem. Abstr.*, **82**, 38228 m (1975).
16) M. Pryszezewska and E. Krzeszowka, *Talonta*, **18**, 638 (1971).
17) F. Freese, H. J. Jasper, and G. Don Boef, *Talanta*, **17**, 945 (1970).
18) V. I. Suprunovich, Zh. B. Kulikovskaya, and S. N. Pirozhok, *Zavod. Lab.*, **45**, 293 (1979).
19) E. F. Denilenko and Yu. I. Usatenko, *Khim. Tekhnol. (Kharkov)*, **18**, 164 (1971).
20) O. A. Songina, V. A. Zakharov, I. M. Bessarabova, P. Rakhimzhanov, and I. I. Safonov, *Zh. Anal. Khim.*, **27**, 1121 (1972).
21) V. V. Voloshina, Yu. I. Usatenko, and A. M. Arishkevich, *Zavod. Lab.*, **36**, 530 (1970).
22) D. D. Perrin, "Masking and Demasking of Chemical Reactions," Wiley-Interscience, New York (1970).