122 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 122—126 (1976) [Vol. 49, No. 1

Analytical Application of Catalytic Polarographic Current of Nickel(II) in Acidified Thiocyanate Solutions Containing Cobalt(II)

Eiki ITABASHI and Ikuko YUSA
Miyagi University of Education, Aoba, Aramaki, Sendai 980

(Received June 6, 1975)

Simple and sensitive methods have been developed for the determination of nickel(II), based on the catalytic polarographic current in acidic thiocyanate solution in the presence and absence of cobalt(II). The basis of the methods and the effect of variables have been investigated and elucidated. In the absence of cobalt(II), thiocyanate solution containing large amounts of hydrogen ions serves a supporting electrolyte, while an acidic thiocyanate solution containing tetra-*n*-butylammonium salts is suitable for the determination of nickel(II) in the presence of cobalt(II). These methods are applicable to the determination 2×10^{-6} M nickel(II) in the presence and absence of 1×10^{-3} M cobalt(II).

Polarographic as well as anodic stripping methods have been applied for the analysis of nickel(II). It has been found that pyridine is a good supporting electrolyte for the polarographic simultaneous determination of nickel(II) and cobalt(II). Thiocyanate electrolyte serves a good supporting electrolyte when only nickel(II) is to be determined in neutral solution.[1,2] The anodic stripping method has been applied by employing sodium thiocyanate as a supporting electrolyte;[3] however, thiocyanate electrolyte is not suitable for the anodic stripping analysis of nickel, because during the reduction of nickel(II) at both mercury and platinum electrodes the reduction of thiocyanate ions takes place with the formation of sulfides and cyanides.[4–7]

The polarographic reduction of nickel(II) in acidified thiocyanate solution in the presence and absence of tetraalkylammonium salts has previously been reported to exhibit a catalytic wave having the shape of a "maximum".[8] The mechanism of this catalytic wave was thought to involve the cyclic regeneration of the electroactive nickel(II) according to the following reaction sequence:[5,8]

$$\mathrm{NiNCS^{+}_{ads}} + 2\mathrm{e} \xrightarrow{\text{fast}} \mathrm{Ni(0)NCS^{-}}$$

$$\mathrm{Ni(0)NCS^{-}} + 3\mathrm{H^{+}} \xrightarrow{\text{slow}} \mathrm{Ni^{2+}} + \mathrm{HCN} + \mathrm{H_2S}$$

The cyclic regeneration of nickel(II) accounts for the enhancement of the limiting current. Hydrogen ions act as a neutralizing agent of the reduction products of thiocyanate ion, cyanide and sulfide ions. This catalytic wave is usually sensitive and selective. This immediately suggests the use of the present catalytic wave to determine the concentration of nickel(II). Previously polarographic catalytic current based on the oxidation-reduction,[9,10] dispropotionation,[11] hydrogen reduction wave,[12,13] and pre-wave[14,15] have been employed successfully for the determination of metal ions and nitrogen- or sulfur-containing organic compounds. The present paper reports on some analytical applications utilizing the catalytic current of nickel(II) in the presence and absence of cobalt(II).

Experimental

Chemicals. Nickel(II) perchlorate[16] and cobalt(II) perchlorate[17] were prepared and recrystallized using the procedures given in literatures. Tetra-*n*-butylammonium perchlorate(n-$\mathrm{Bu_4NClO_4}$) was prepared by neutralizing a 40% tetra-*n*-butylammonium hydroxide solution with perchloric acid and recrystallized several times from ethyl alcohol, and then dried in a vacuum oven at 80 °C for 20 h. Extra pure grade sodium thiocyanate and perchloric acid were used. All the other chemicals were of chemical grade without further purification. Redistilled water was used and all solutions were deaerated with high-purity nitrogen.

Instrumentation and Electrode Assembly. Direct current (DC) polarographic experiments were carried out with a potentiostat constructed locally with operational amplifiers.[18] Polarograms were recorded with a X-Y recorder.

Two capillaries were used throughout this work. The rate of flow of mercury (m) and the drop time (t) of capillary I were 1.49_6 mg/s and 5.42 s, respectively, measured in deaerated 0.5 M NaCl solution under an applied pressure of 55 cm at -0.65 V *vs.* SCE. Capillary II had the characteristics $m=1.33_1$ mg/s and $t=4.95$ s, in deaerated 0.5 M $\mathrm{NaNO_3}$ solution under an applied pressure of 40 cm at -0.56 V *vs.* SCE. Capillaries I and II were employed for the experiments of methods I and II, respectively.

The counter electrode was a platinum spiral electrode which was connected to the electrolytic solution through a glass sinter. The potential of the DME was measured against a saturated calomel electrode (SCE) which was connected to the test solution through a Luggin capillary with a pair of sintered glass discs.

Procedure for the Determination of Nickel(II) in the Presence of Cobalt(II). Because n-$\mathrm{Bu_4NClO_4}$ is slightly soluble in water, the electrolytic solutions are usually prepared as follows Into a 25 ml volumetric flask, add 68 mg (8 mM) or 85 mg (10 mM) of n-$\mathrm{Bu_4NClO_4}$, and then pour in 10 ml of 2.5 M NaSCN solution. Dissolve n-$\mathrm{Bu_4NClO_4}$ in thiocyanate solution by shaking gently. After dissolution of n-$\mathrm{Bu_4NClO_4}$ in thiocyanate solution, add perchloric acid and nickel (II) or cobalt(II) solution containing nickel(II), and dilute to 25 ml with distilled water and mix well. Prior separation of the precipitate of $(n\text{-}\mathrm{Bu_4N})_2\,[\mathrm{Co(NCS)_4}]$ is used when the solution contains more than 2×10^{-4} M cobalt(II). Pour the solution into a 100 ml centrifuge tube and then centrifuge for 30 min at 3500 rpm. Transfer the solution into the cell and then analyze the solution by the conventional DC polarographic method.

Treatment of Data. The catalytic wave of nickel(II) in acidic thiocyanate solution appears as a maximum wave. The value of peak current denoted as i_p is measured at the peak potential of the maximum wave. All values are corrected for the residual current or for the limiting current caused to the reduction of metal ions such as iron(III) and copper(II), which are reduced at potentials less negative than nickel(II). The latter way can be done by extrapolation of the linear flat portion of the limiting current before the maximum wave rises. The concentration of nickel(II) is evaluated with reference to a suitably prepared calibration curve.

Results and Discussion

In the Absence of Cobalt(II) [Method I]. Figure 1 shows the DC polarogram obtained in 0.5 M thiocyanate solution containing 2×10^{-5} M nickel(II) and 0.14 M $HClO_4$. Nickel(II) in acidic thiocyanate solution gives a peak current rather a limiting plateau. This peak occurs at about −0.82 V *vs.* SCE. The rise in current at potentials more negative than −1.0 V is attributed to the direct reduction of hydrogen ions. In the absence of nickel(II), hydrogen ions in 0.5 M thiocyanate solution containing 0.14 M $HClO_4$ are reduced at potentials more negative than about −0.87 V.

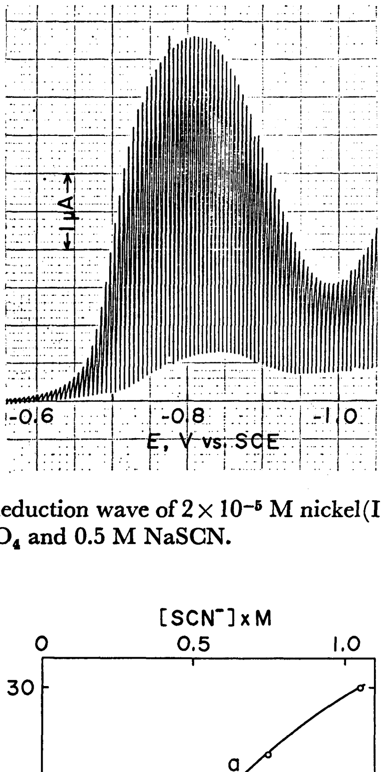

Fig. 1. Reduction wave of 2×10^{-5} M nickel(II) in 0.14 M $HClO_4$ and 0.5 M NaSCN.

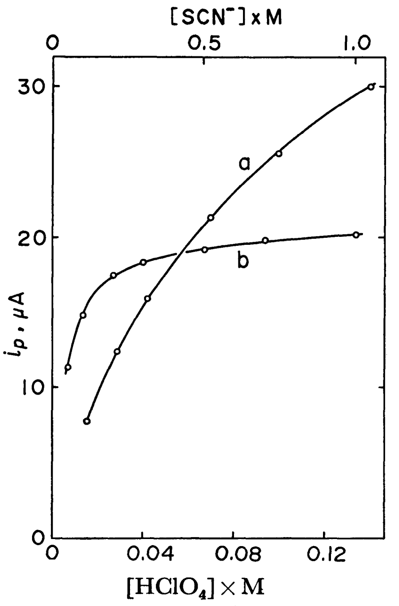

Fig. 2. Effect of concentrations of $HClO_4$ (a) in 0.5 M NaSCN, and NaSCN (b) in 0.056 M $HClO_4$ on the peak current of 1×10^{-4} M nickel(II).

The effect of the concentrations of thiocyanate and hydrogen ions on the peak current was studied to determine its applicability as a method for determing small amounts of nickel(II) polarographically. Figure 2 presents the relationships between the peak current and the concentrations of thiocyanate and hydrogen ions. The peak current increases in height with increase in hydrogen ion concentration. With further addition of $HClO_4$ above 0.2 M, the maximum wave appears as a shoulder on the hydrogen reduction wave. The concentrations 0.14 M in $HClO_4$ and 0.5 M in NaSCN have been selected for further experiments.

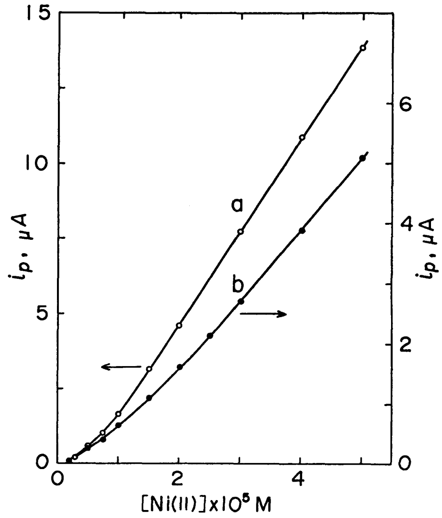

Fig. 3. Plots of i_p *vs.* nickel(II) concentration in 0.5 M NaSCN solution containing 0.14 M $HClO_4$ (a), and in 1.0 M NaSCN solution containing 7×10^{-3} M $HClO_4$ and 8×10^{-3} M n-Bu_4NClO_4 (b).

The height of the peak current as a function of the nickel(II) concentration is shown by curve a of Fig. 3. Two distinct portions are present on the curve. The first part at which the rise in the peak current with nickel(II) concentration is greater than linear extends from 2×10^{-6} to 1.5×10^{-5} M. The second portion at which the peak current is proportional to the nickel(II) concentration is observed in the concentration range from 2×10^{-5} to 1×10^{-4} M. This inflection on the calibration curve could indicate that the mechanism of the catalytic wave involves the sequence of reactions and a rate-determing step of the overall process changes over a wide range of nickel(II) concentration. The present method is suited for the determination of 2×10^{-6} to 1×10^{-4} M nickel(II) in the absence of cobalt(II).

In the Presence of Cobalt(II) [Method II]. With analysis of mixures, interference is always a possibility with any technique. The effect of cobalt(II) on the catalytic maximum wave of nickel(II) in acidic thiocyanate solution is presented in Fig. 4. These polarograms are drawn as the line through the maximum current observed just before the fall of a mercury drop. The peak height decreases with increase in cobalt(II) concentration. This may be due to the adsorption of

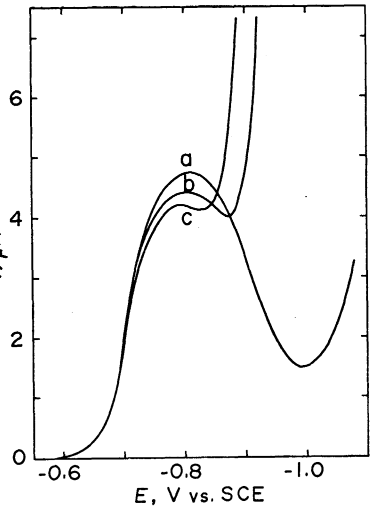

Fig. 4. Effect of cobalt(II) on the reduction waves of 2×10^{-5} M nickel(II) in 0.14 M $HClO_4$ and 0.5 M NaSCN.
[Co(II)]: a) 0, b) 2×10^{-4}, c) 5×10^{-4} M.

cobalt(II)-thiocyanate complexes. Cobalt(II) in thiocyanate solution containing perchloric acid or acetate buffer also exhibits a catalytic maximum wave.[19] This catalytic wave appears in the potential region where cobalt(II) exhibits a pre-wave which arises at less negative potentials than those for the usual hydrated cobalt(II) reduction wave. The catalytic current of cobalt(II) in acidic thiocyanate solution has a mixed adsorption-surface character.[19] If nickel(II)- and cobalt(II)-thiocyanate complexes are coadsorbed at the same potential region, the catalytic current of nickel(II) decreases because of decreasing adsorption of nickel(II)-thiocyanate complexes and hence of decreasing concentration of the active metallic nickel at the electrode surface.

It is therefore necessary to separate cobalt(II) from the solution containing nickel(II). Cobalt(II) in thiocyanate solution containing large cations such as tetraalkylammonium or tetraphenylarsonium ions yields the precipitate having the composition of $(Cat)_2$-$[Co(NCS)_4]$, where Cat^+ is tetra-alkylammonium or -phenylarsonium ion.[20–22]

Of the many tetraalkylammonium salts investigated, n-Bu_4NClO_4 was the most suitable for the separation of cobalt(II) from the thiocyanate solution containing nickel(II).

The catalytic reaction of nickel(II) in acidic thiocyanate solution is also enhanced by the presence of various kinds of tetraalkylammonium ions.[5,8] Figure 5 shows the reduction wave of nickel(II) in acidic thiocyanate solution containing n-Bu_4NClO_4. The values of peak current of 5×10^{-5} M nickel(II) in 7×10^{-3} M $HClO_4$ and 1.0 M NaSCN solutions in the presence and absence of 8×10^{-3} M n-Bu_4NClO_4 are 5.02 and 2.45 μA, respectively.

Acceleration of the catalytic reaction of nickel(II) by the presence of n-Bu_4N^+ ions could be the result of the inhibition of the amalgamation of electrodeposited metallic nickel. The amalgamation of the deposited iron-group metals is known to be inhibited by the presence of some surface-active substances.[23–25]

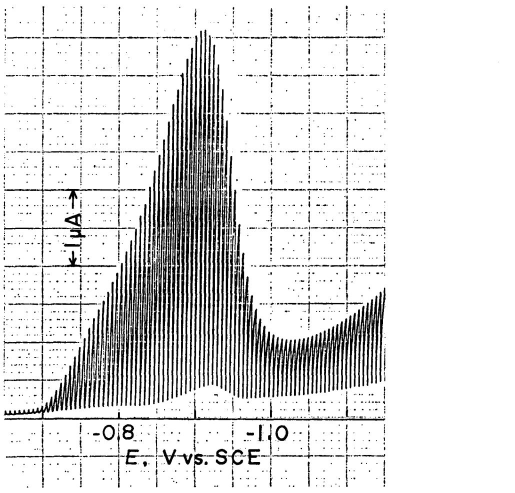

Fig. 5. Reduction wave of 5×10^{-5} M nickel(II) in 7×10^{-3} M $HClO_4$, 8×10^{-3} M n-Bu_4NClO_4 and 1.0 M NaSCN.

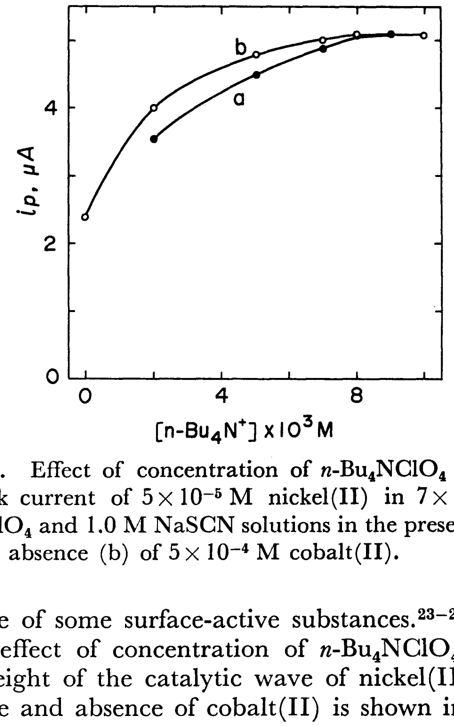

Fig. 6. Effect of concentration of n-Bu_4NClO_4 on the peak current of 5×10^{-5} M nickel(II) in 7×10^{-3} M $HClO_4$ and 1.0 M NaSCN solutions in the presence (a) and absence (b) of 5×10^{-4} M cobalt(II).

The effect of concentration of n-Bu_4NClO_4 on the peak height of the catalytic wave of nickel(II) in the presence and absence of cobalt(II) is shown in Fig. 6. The peak current reaches a limiting value as the concentration of n-Bu_4NClO_4 increases. The difference between the peak currents in the presence and absence of cobalt(II) at lower concentrations of n-Bu_4NClO_4 is associated with a decrease in concentration of n-Bu_4N^+ ions in the bulk of solution.

Tetra-n-butylammonium ions in thiocyanate solution containing cobalt(II) are partially consumed for the precipitation of cobalt(II)-thiocyanate complex in the form of $(n\text{-}Bu_4N)_2[Co(NCS)_4]$. The peak current of nickel(II) in thiocyanate solution containing 8×10^{-3} M n-Bu_4NClO_4 remains unchanged with further addition of $HClO_4$ above 5×10^{-3} M, as shown in Fig. 7. Figure 8 presents the dependence of the peak current on the thiocyanate concentration. With further addition of NaSCN above 1.0 M, the peak current reaches a limiting value.

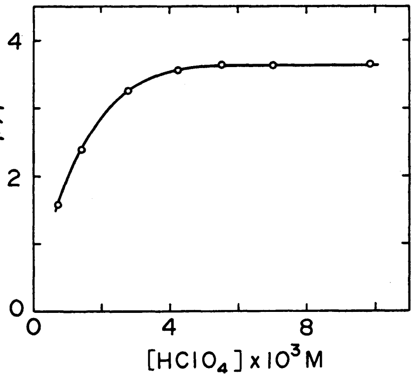

Fig. 7. Effect of concentration of $HClO_4$ on the peak current of 5×10^{-5} M nickel(II) in 8×10^{-3} M n-Bu_4NClO_4 and 0.5 M NaSCN.

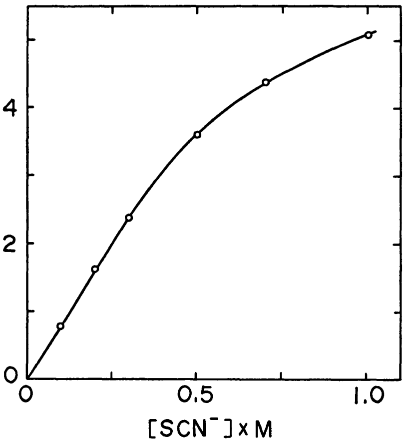

Fig. 8. Effect of thiocyanate concentration on the peak current of 5×10^{-5} M nickel(II) in 7×10^{-3} M $HClO_4$ and 8×10^{-3} M n-Bu_4NClO_4.

As a result of the experiments described above, it is possible to select the conditions and established a procedure for the determination of nickel(II) in the presence of cobalt(II). The experiments were performed with the solutions containing 7×10^{-3} M $HClO_4$, 8×10^{-3} M n-Bu_4NClO_4 and 1.0 M NaSCN. Over the entire range of nickel(II) between 2×10^{-6} and 2×10^{-4} M, the maximum waves were similar to that shown in Fig. 5. The present method has also two distinct portions on the calibration curve, as shown by curve b of Fig. 3. The first part at which the curve is a non-linear extends from 2×10^{-6} to 2×10^{-5} M nickel(II), and the second part at which the curve is a linear is observed in the nickel(II) concentration between 2.5×10^{-5} and 2×10^{-4} M. The quantity of nickel(II) in the presence of cobalt(II) was estimated from the calibration curve. Data compiled in Table 1 verify that in the presence of large excess of cobalt(II) nickel(II) can be accurately determined within expected polarographic precision. When the solution contains 1×10^{-3} M cobalt(II) and nickel(II) of 2×10^{-5} M or greater, it is desirable to employ 10×10^{-3} M n-Bu_4NClO_4 instead of 8×10^{-3} M. With 1×10^{-3} M cobalt(II) present, approximately 2×10^{-3} M n-Bu_4N^+ ions are consumed for the precipitation reaction of cobalt(II)-thiocyanate compound in the bulk of solution.

Table 1. Analysis of nickel(II)[a]

[n-Bu_4NClO_4] M×10^3	[Co(II)] M×10^3	[Ni(II)], M×10^6 Taken	Found[b]	Derivation M×10^6
8	1.0	2.0	1.9	−0.2—+0.1
8	0.5	5.0	5.1	−0.3—+0.1
8	1.0	20.0	19.8	−0.5—+0.4
10	1.0	20.0	19.8	−0.3—+0.2
8	0.5	50.0	49.3	−1.2—−0.7
10	0.5	50.0	50.2	−0.4—+0.5

a) Solution contains 7×10^{-3} M $HClO_4$ and 1.0 M NaSCN. b) Average of four replicate determinations on the different solutions.

Effect of Foreign Ions. Methods I and II described in this paper offer higher sensitivity than those being available in the literature.[2] Both methods were applied in a variety of situations to evaluate their effectiveness by employing the solutions containing 2×10^{-5} M nickel(II) and foreign ions.

In method I, the presence of 2×10^{-4} M aluminum(III), iron(III), zinc(II), and lead(II) is tolerated. An error of 3% or greater occurs with these foreign ions of 5×10^{-4} M present. Chromium(III), copper(II) and cadmium(II) interfere in method I. Chromium(III) reduces the height of the peak current of nickel(II). An acidic thiocyanate solution containing nickel(II) and cadmium(II) gives a single round maximum wave in the potential region between −0.6 and −1.0 V. Copper(II) in acidic thiocyanate solution exhibits an ill-defined reduction wave. Halide, nitrate, sulfate, and oxalate ions are tolerated up to approximately 0.01 M.

In method II, chromium(III) and aluminum(III) are tolerated. Iron(III), copper(II), zinc(II), cadmium(II), and lead(II) are precipitated in thiocyanate solution containing n-Bu_4N^+ ions. Copper(II), cadmium(II), and zinc(II) are tolerated at low concentration than 2×10^{-4} M. Iron(III) and lead(II) are tolerated up to 5×10^{-5} M. Anions such as bromide, iodide, sulfate, nitrate, and oxalate ions which are in part associated with n-Bu_4N^+ ions are tolerated up to 5×10^{-3} M.

In conclusion, method II is more sensitive than method I. Method II is applicable for the routine analysis of nickel(II) in various cobalt compounds by employing the calibration curve prepared carefully, although the calibration curve is a non-linear.

The authors thank the Ministry of Education for the financial support.

References

1) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **13**, 77 (1941).

2) J. M. Dale and C. V. Banks, "Treatise on Analytical Chemistry," Vol. 2, Part II-A, ed. by I. M. Kolthoff and P. J. Elving, Wiley-Interscience, New York (1962), p. 377.

3) M. M. Nicholson, *Anal. Chem.*, **32**, 1058 (1960).

4) H. Shirai, *Nippon Kagaku Zasshi*, **85**, 322 (1964).

5) E. Itabashi and S. Ikeda, *J. Electroanal. Chem.*, **27**, 243 (1970).

6) T. Hurlen and E. Eriksrud, *ibid.*, **54**, 331 (1974).

7) T. Krogules, A. Barański, and Z. Galus, *J. Electroanal. Chem.*, **57**, 63 (1974).

8) E. Itabashi, *ibid.*, **60**, 285 (1975).

9) I. M. Kolthoff and E. P. Parry, *J. Amer. Chem. Soc.*, **73**, 5315 (1951).

10) T. A. O'Shen and G. A. Parker, *Anal. Chem.*, **44**, 184 (1972).

11) W. E. Harris and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **68**, 1175 (1946).

12) R. Brdička, *Collect. Czech. Chem. Commun.*, **5**, 238 (1933).

13) J. Heyrovský and J. Kůta, "Principle of Polarography," Academic Press, New York (1966), p. 407.

14) H. B. Mark, Jr. and C. N. Reilley, *Anal. Chem.*, **35**, 195 (1963).

15) L. R. McCoy and H. B. Mark, Jr., *ibid.*, **37**, 591 (1965).

16) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

17) N. A. Matwiyoff and S. V. Hooker, *ibid.*, **6**, 1127 (1967).

18) E. Itabashi and K. Oikawa, *Ann. Rept. Res. Inst. Sci. Educ., Miyagi Univ. Educ.*, **8**, 17 (1973).

19) E. Itabashi and M. Tan, *J. Electroanal. Chem.*, **60**, 299 (1975).

20) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715, 823 (1965).

21) A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965).

22) H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, **71**, 1138 (1967).

23) V. F. Ivanov and Z. A. Iofa, *Russ. J. Phys. Chem., Engl. Trans.*, **36**, 571 (1962); **38**, 1026 (1964).

24) I. M. Kolthoff and P. Mader, *Anal. Chem.*, **41**, 924 (1969).

25) E. Itabashi and S. Ikeda, *J. Electroanal. Chem.*, **36**, 189 (1972).