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Polarographic Characteristics of Vanadium Complexed with Ethylenediamine Tetraacetic Acid

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The polarographic behavior of the various oxidation states of vanadium complexed with ethylenediamine tetraacetic acid has been studied over the *p*H range 5–12.6. The vanadous and vanadic complexes give single reversible waves over the entire *p*H range. In both cases the half-wave potential was found to be independent of *p*H from *p*H 5–8.5 and equal to −1.27 v. *vs.* S.C.E.; at higher *p*H the half-wave potential is *p*H dependent. The vanadyl–Versene complex shows a characteristic prewave believed to be the rate-controlled reduction of +4 to +3 vanadium followed by the "main wave," the reduction of +3 to +2. For these three oxidation states the half-wave potential was found to be independent of the concentration of Versene. Complexes of these three oxidation states should be very useful for the polarographic determination of vanadium when other ions interfere with the non-complexed wave. Polarograms of +5 vanadium–Versene show two waves in acid solutions. The first wave is the reduction of +5 to +4 vanadium, the second is the reduction of +4 to +2 vanadium. In basic solutions only one irreversible wave is observed which is, apparently, the reduction of +5 to +2 vanadium.

The present study was undertaken in order to determine the polarographic behavior of the several oxidation states of vanadium complexed with Versene (sodium salts of ethylenediamine tetraacetic acid). Versene solutions form chelate complexes with a number of metallic ions. Kolthoff and Auerbach[1] have investigated the iron–Versene system, and polarographic studies of Versene complexes of a number of other elements are being carried on in these laboratories at the present time and will be reported shortly. Lingane[2] and Lingane and Meites[3] have made comprehensive studies on the various oxidation states of vanadium in non-complexing and in oxalate solutions, respectively. No previous study has been reported in the literature on the vanadium–ethylenediamine tetraacetic acid complex.

Experimental

Polarograms were recorded according to usual technique[4] with a Sargent Model XXI automatically recording polarograph. An H-type cell using a saturated calomel electrode as anode was used. Nitrogen, purified by bubbling through a chromous solution, was used to remove oxygen from all solutions prior to taking polarograms. Solutions of supporting electrolyte to which vanadous solutions were to be added were all bubbled for a minimum of 30 minutes. Purified nitrogen was passed over the solution during the actual polarographic run. All measurements were made with the cell in a water thermostat at 25.0 ± 0.1°. All *p*H values were measured with a Beckman Model H2 *p*H meter. The polarographic cell was arranged in such a way that the glass electrode of the *p*H meter could be left in the cell thus lessening the chance of air oxidation when *p*H values were taken. The *p*H was taken before and after each polarogram. The drop time of the capillary was 5.02 sec. on open circuit and 4.20 sec. at an applied potential of −1.5 volts at which most measurements of diffusion currents were made. The rate of flow, *m*, was 2.437 mg. sec.$^{-1}$. Correction was made for residual currents in determining all diffusion current data. The concentration of Versene was 0.1 *M* in all cases except where noted. Maximum suppressors are not required in these solutions.

Chemically pure ammonium metavanadate (A. D. Mackay) served as a source of +5 vanadium. A 0.02095 *M* stock solution was prepared by dissolving the required amount of the salt in 50 ml. of 5 *F* sodium hydroxide. One hundred milliliters of 6 *F* hydrochloric acid was added slowly with stirring. The solution was then made up to one liter and standardized by the method of Ramsey.[5]

A stock solution of vanadyl chloride was prepared by bubbling sulfur dioxide through an acidic solution of ammonium vanadate. The vanadyl solution thus formed was freed of excess sulfur dioxide by boiling and by bubbling nitrogen through the solution. A portion of the solution was tested for complete reduction to +4 vanadium by addition of iodide ion. No iodine could be observed in a carbon tetrachloride layer. The vanadyl solution was standardized by the permanganate method.[6]

Vanadic solutions were prepared by two different methods. Method I consisted of the electrolytic reduction of 0.02095 *M* +5 vanadium with a Heathkit Electrolytic Analyzer.[7] The +5 vanadium solution was placed in an unglazed porous cup and the cup was immersed in a 2 *M* sulfuric acid solution so that the height of the sulfuric acid was exactly level with that of the vanadium solution. A platinized platinum cathode was immersed in the vanadium solution and a platinum anode was placed in the acid solution. Electrolysis was continued for four hours (voltage, 5 volts; current, 0.5 amp.). At the end of this time a clear, light green solution was obtained which was found to be + 3 vanadium by polarographic analysis. The solution was stored under nitrogen and was standardized under nitrogen with permanganate. This solution was found to be slightly more concentrated than the vanadyl solution due to the fact that water was decomposed in the electrolysis.

Method II for the preparation of +3 vanadium was equally useful. Amalgamated zinc was shaken with +5 vanadium under an atmosphere of carbon dioxide. When the solution became violet indicating the presence of +2 vanadium, the solution was transferred to a vessel which contained a piece of platinized platinum. The vanadous solution was oxidized to a vanadic solution with an evolution of hydrogen. This vanadic solution was stored under nitrogen. Standardization of this solution by permanganimetric titration showed the concentration of +3 vanadium to be in very close agreement with the values obtained for +4 and +5 vanadium.

Vanadous chloride solutions were prepared by reducing the 0.02095 *M* +5 vanadium solution with amalgamated zinc. The yellow solution first became blue, then light green, and finally became violet. This solution was then sent through a Jones reductor to ensure complete reduction. The receiving apparatus was flushed first with carbon dioxide, then with nitrogen, and the Jones reductor was connected directly to the storage flask. The liquid was stored under a slight pressure of nitrogen. A five ml. micro-buret was connected directly to the storage flask. Polarograms of this solution in 0.1 *M* potassium chloride give a completely anodic wave with half-wave potential −0.500 v. *vs.* S.C.E. which is in agreement with the value obtained by Lingane.[2] This vanadous solution was standardized using the method

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[1] I. M. Kolthoff and C. Auerbach, THIS JOURNAL, **74**, 1452 (1952).

[2] J. J. Lingane, *ibid.*, **67**, 182 (1945).

[3] J. J. Lingane and L. Meites, Jr., *ibid.*, **69**, 1021 (1947).

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

[5] J. B. Ramsey, THIS JOURNAL, **49**, 1138 (1927).

[6] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 359.

[7] P. S. Farrington and R. L. Pecsok, *J. Chem. Ed.*, in press.

of Meites.[8] The result was in very close agreement with values obtained for the other valence states of this solution.

A 0.25 *M* Versene stock solution was prepared from Eastman Kodak Co. white label ethylenediamine tetraacetic acid (disodium salt). The Versene solution was standardized by titrating a known volume with standarized sodium hydroxide acidimetrically.

Results and Discussion

A series of polarograms of 5.0 millimolar zinc in 0.1 *M* Versene solution was taken at *p*H values of 6.0 to 12.0 to determine if zinc would interfere with the vanadium determination. No wave was found for zinc in this *p*H range.

+2 Vanadium.—It was found that the vanadous–Versene complex is extremely sensitive to air oxidation as was also found to be the case for the ferrous–Versene complex by Kolthoff and Auerbach.[1] A single reversible anodic wave is produced with $E_{1/2}$ of −1.270 volts *vs.* S.C.E. at *p*H values less than 8.3. Oxidation proceeds to +3 vanadium, and no other wave was found which indicates higher oxidation or reduction at the dropping mercury electrode. Curve A of Fig. 1 shows a typical vanadous wave. It will be noted that the wave is not entirely anodic which indicates the presence of a small amount of +3 vanadium.

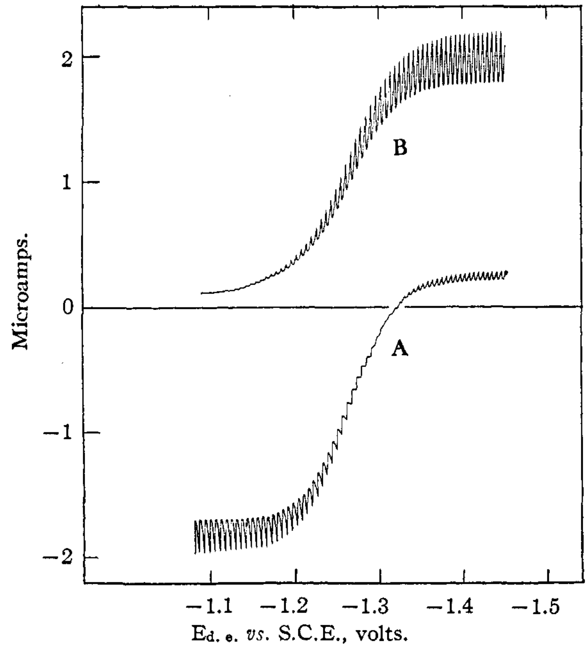

Fig. 1.—Typical polarograms of +2 and +3 vanadium-Versene: a, 0.806 millimolar +2 vanadium in 0.1 *M* Versene at *p*H 7.00; b, 0.806 millimolar +3 vanadium in 0.1 *M* Versene at *p*H 7.18.

A series of polarograms was taken to find the effect of *p*H on the half-wave potential of the vanadous–Versene complex. The total concentration of Versene was kept at 0.1 *F*. The values obtained are plotted in Fig. 2 in which the *p*H is corrected for sodium ion. At *p*H values less than about 5, hydrogen waves obscure the vanadium wave. It will be noted that two straight lines can be drawn through the experimental points. The slopes of these lines are 0.00 and 0.058 volt/*p*H. This indicates that the half-wave potential is independent of *p*H from about *p*H 5 to 8.3. The electrode reaction in this region is therefore

$$VY^{=} = VY^{-} + e^{-} \qquad (1)$$

where ethylenediamine tetraacetic acid is symbolized by H_4Y.

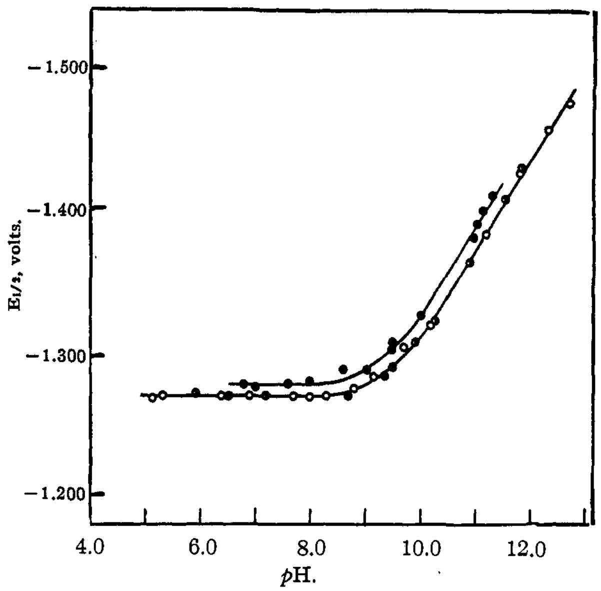

Fig. 2.—Effect of *p*H on $E_{1/2}$: ○, +2 vanadium; ◑, +3 vanadium; ●, $E_{1/2}$ of the "main-wave" of +4 vanadium in 0.1 *M* Versene.

From about *p*H 10 to 12.6 the slope was found to be 0.058 which is equivalent to one hydrogen (or hydroxide) ion entering into the reaction per molecule of complex. The reaction is therefore

$$VY^{-} + OH^{-} = V(OH)Y^{=} + e^{-} \qquad (2)$$

The effect of concentration of Versene on the half-wave potential was next determined. The concentration of zinc was determined polarographically using 1 *M* ammonia–ammonium chloride as supporting electrolyte. The vanadium was precipitated in this solution and the diffusion current of the zinc was compared with that of a known solution. The concentrations of the zinc–Versene complex and vanadous–Versene complex were subtracted from the amount of Versene added in determining the concentration of free Versene. Vanadous solutions were added to solutions of varying concentrations of Versene. The ionic strength was adjusted to *ca.* 0.1 *M* with potassium chloride. The final *p*H was adjusted to lie between 6.2 and 6.7. It was found that the half-wave potential of the vanadous–Versene complex is independent of the concentration of Versene from 0.00087 *M* to 0.194 *M* Versene and was in each case −1.270 v. *vs.* S.C.E. At very low concentrations of Versene two waves were observed—one with $E_{1/2}$ at *ca.* −0.5 volt, and the other with $E_{1/2}$ at *ca.* −1.27 volts. These two waves correspond to the free vanadous ion and the complexed ion. The independence of half-wave potential on concentration of complexing reagent indicates that the number of molecules of complexing agent coördinated with the oxidized and reduced states is the same and is, in this case, equal to one.

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(8) L. Meites, *ibid.*, **27**, 458 (1950).

+3 Vanadium.—Polarograms of the vanadic–Versene complex give a single reversible cathodic wave, reduction proceeding to +2 vanadium. The vanadic–Versene complex is easily oxidized by air to +4 vanadium, but is much more stable than the vanadous–Versene complex. No anodic wave indicating oxidation to +4 vanadium was observed when complexed by Versene.

A series of polarograms was taken to observe the dependence of the half-wave potential on *p*H. It was found, as might be expected, that the curve of $E_{1/2}$ *vs.* *p*H for +3 vanadium–Versene was identical with $E_{1/2}$ *vs.* *p*H for +2 vanadium–Versene (Fig. 2). Thus the half-wave potential of the +3 vanadium complex was found to be independent of *p*H from values of about *p*H 5 to 8.5. This indicates the electrode reaction is the reverse of reaction (1). At *p*H values above 10 the slope of $E_{1/2}$ *vs.* *p*H indicates that one hydroxyl group enters into the electrode reaction. Thus the electrode reaction is the reverse of reaction (2). A typical vanadic–Versene wave at *p*H 7.18 is shown in Fig. 1. The equation[9]

$$(E_{1/2})_c - (E_{1/2})_s = -0.0591 \log K_{ox}/K_{red}$$

where $K_{ox} = (VY^-)/(V^{+3})(Y^{-4})$, $K_{red} = (VY^{-2})/(V^{+2})(Y^{-4})$, and $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complexed and simple ions, respectively, may be used to calculate the ratio K_{ox}/K_{red} in the *p*H range 5 to 8.5. $(E_{1/2})_s$ is equivalent to the standard potential of the non-complexed vanadic–vanadous couple reported by Jones and Colvin[10] to be −0.51 v. *vs.* the S.C.E., determined by ordinary potentiometric methods with a large stationary mercury electrode. $(E_{1/2})_c$ is −1.27 v. *vs.* the S.C.E. The value calculated is $10^{12.9}$, which shows the very high stability of the vanadic–Versene complex as compared to the vanadous–Versene complex. It is not possible to obtain the absolute value of either K_{ox} or K_{red} from these measurements alone.

The +2 vanadium–Versene complex is so extremely sensitive to oxidation that we were unable to obtain a completely anodic wave. In order to measure its diffusion current constant, which is significantly different from that of the +3 complex, an indirect method was used. A small amount of the +2 vanadium stock solution was added to an air-free 0.1 *M* Versene supporting electrolyte, yielding a solution 0.806 millimolar in total vanadium. The polarogram of this solution was 92% anodic, indicating that approximately 8% of the vanadium had been oxidized to the +3 state. The remaining +2 vanadium was oxidized in small increments by blowing gently across the top of the cell. The solution was stirred with nitrogen after each increment of oxidation and a polarogram recorded. The total diffusion current of the composite wave is a linear function of the per cent. of +2 vanadium present (determined from the fraction of the wave which was anodic). Extrapolation to 100% and 0% +2 vanadium yields values of the diffusion current from which the diffusion current constant of the +2 and +3 vanadium–Versene complex can be calculated: 1.10 ± 0.02 and 1.20 ± 0.02, respectively.

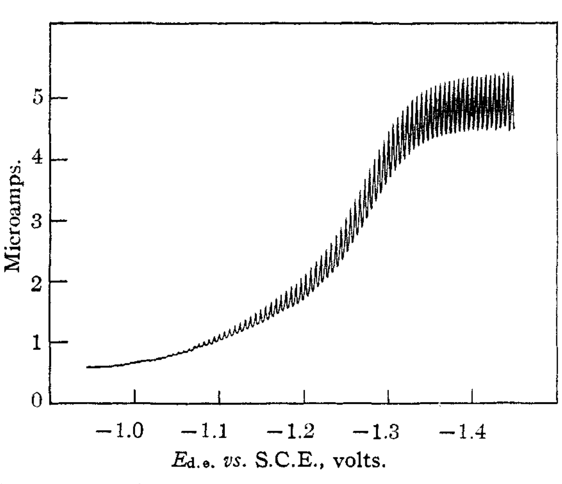

Fig. 3.—Typical polarogram of vanadyl–Versene, 0.806 millimolar +4 vanadium in 0.1 *M* Versene at *p*H 9.54.

+4 Vanadium.—The polarogram of the vanadyl–Versene complex is an irreversible wave with a characteristic prewave (Fig. 3). Reduction proceeds to +2 vanadium. Lingane and Meites[8] observed that vanadyl ion gave a single well-defined wave with half-wave potential of −0.85 v. *vs.* S.C.E. in 0.1 *N* sulfuric acid. However, in less acidic solutions these authors observed a shift to more negative potentials and a prewave similar to that obtained by the present authors. They postulated that the prewave was due to the rate controlled reduction of a species, possibly $VOOH^+$, formed by hydrolysis of VO^{++}. It was observed by us that in the vanadyl–Versene complex the prewave always extended to exactly one-half the limiting current before the "main wave" began to form. This leads us to suspect that the prewave is due to the reduction of +4 vanadium to +3 vanadium and the "main wave" due to the reduction of +3 vanadium to +2 vanadium. This postulation was supported in the following ways. Various mixtures of +3 and +4 vanadium were prepared with 25, 50 and 75% +4 vanadium. These mixtures, complexed by Versene, were then examined polarographically. In each case a single wave preceded by a prewave was obtained, and in each case by doubling the maximum current of the prewave and dividing this by the total limiting current, the percentage of +4 vanadium could be determined with an accuracy of ±5%. Since no other wave was introduced by the addition of +3 vanadium and the only change was the enlargement of the main wave, the main wave must be due to the reduction of +3 to +2 vanadium. Still further proof of this proposal is given by the fact that a plot of $E_{3/4}$($E_{1/2}$ of the main wave) *vs.* *p*H for +4 vanadium gave a curve whose points lie very close to the curve for the reduction of +3 to +2 vanadium (Fig. 2).

A series of polarograms of the vanadyl–Versene complex was taken to find the effect of *p*H on the wave. The prewave becomes more distinct as the *p*H is increased. At no *p*H studied by us (*p*H 6.8 to 12.2) was the prewave completely eradicated.

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(9) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

(10) G. Jones and J. H. Colvin, THIS JOURNAL, **66**, 1573 (1944).

However, polarograms at lower *p*H indicate that the prewave may be eradicated at still lower *p*H values as found by Lingane and Meites[3] for the non-complexed vanadyl ion in 0.1 sulfuric acid.

The diffusion current constant measured in the *p*H range 6.8 to 8.6 was found to be 2.20 ± 0.02 for the total wave, which is twice the value for the vanadic–vanadous wave.

Interesting color changes occurred as the *p*H was changed. A 0.01 *M* vanadyl-Versene solution was prepared by diluting a 0.02 *M* vanadyl solution with an equal volume of 0.25 *M* Versene. In acid and neutral solutions the vanadyl–Versene complex is a deeper blue than the uncomplexed ion. The *p*H of the solution was made more basic by addition of a concentrated sodium hydroxide solution. At *p*H 11.2 the blue solution changed sharply to a pink solution. Above *p*H 11.62 the solution changed from pink to a clear brownish-yellow pseudo-solution. An attempt was made to produce the pink solution again by addition of hydrochloric acid. However, addition of hydrochloric acid did not reproduce this pink solution, but instead produced a dark green solution. Centrifuging the brownish-yellow "solution" at high speed for five hours produced a colorless liquid and a small amount of brown precipitate. Polarograms of the pink solution produced the characteristic vanadyl–Versene wave. However, polarograms of the yellow "solution" produced very ill-defined waves or no wave at all. Further work will be carried out on these various states of the vanadyl–Versene complex. These sharp color changes suggest the use of vanadyl–Versene as an indicator in strongly basic solutions.

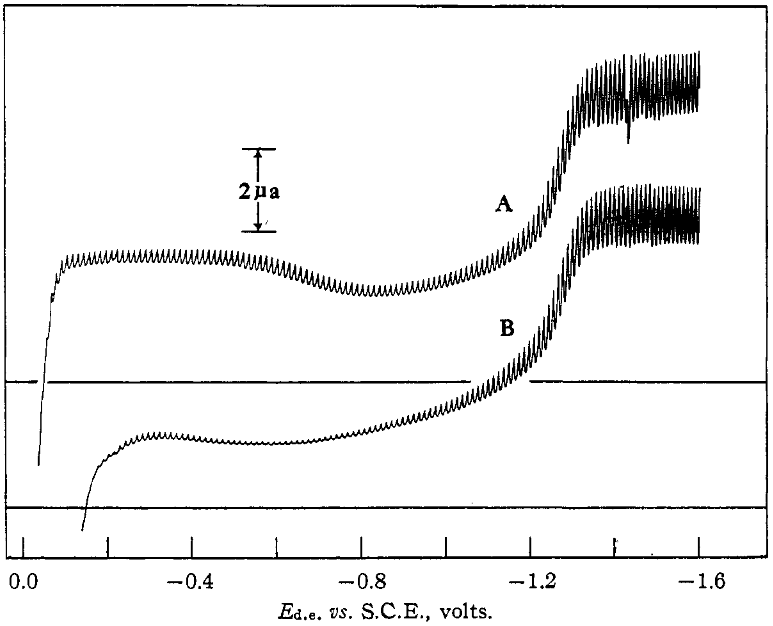

Fig. 4.—Typical polarograms of +5 vanadium–Versene, 0.806 millimolar +5 vanadium in 0.1 *M* Versene: a, *p*H 6.82; b, *p*H 9.08. Horizontal lines indicate the galvanometer zero.

+5 Vanadium.—Polarograms of +5 vanadium in 0.1 *M* Versene solutions produce a current-voltage curve consisting of two waves in acid and slightly basic solutions, and of only one wave in solutions more basic than about *p*H 9.4 (Fig. 4). It will be noted in Fig. 4 that the wave in slightly acid solutions exhibits a flat minimum several tenths of a volt after the plateau has been reached. This peculiar behavior also has been observed by Lingane and Meites[3] working with vanadium–oxalate complexes and is observed in solutions of chloroindic ion in potassium chloride.[11] Non-complexed vanadium does not exhibit this phenomena.[2] This behavior has not, as yet, been explained.

Values of $i_d/h^{1/2}$ for both waves (where *h* is the height of the mercury column corrected for back-pressure) were determined and found to be constant ±3%, at *p*H 6.70 over the range of "*h*" from 37.5 to 75.0 cm. This indicates that the reaction at the electrode is diffusion controlled.

The effect of *p*H on the wave was next studied. At *p*H 6.70 the diffusion current constant of the first wave was found to be 1.00, which corresponds to the one electron reduction of +5 to +4 vanadium. The diffusion current constant of the second wave was found to be 2.19 corresponding to the two electron reduction of +4 to +2 vanadium. As the *p*H became more basic, the first wave became smaller until at a *p*H of *ca.* 9.4 it vanished completely. During the addition of base it was noted that the potential of the lowest point of the minimum shifted toward more positive values. A plot of *p*H *vs.* minimum potential in the *p*H range 6.1 to 9.1 was found to be linear—the minimum potential being 0.126 volt more positive per *p*H unit increase.

At *p*H 9.55 the diffusion current constant of the single irreversible wave was found to be 3.29. This indicates that at *p*H values greater than *ca.* 9.4, +5 vanadium complexed with Versene is reduced directly to +2 vanadium. The half-wave potential of this wave is about −1.22 volts.

Since the diffusion current constant of both waves of the +5 vanadium–Versene complex vary with *p*H, we do not recommend this oxidation state for practical polarographic analysis, but instead recommend the prior reduction to one of the other oxidation states by any of the methods given.

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(11) Reference 4, page 274.