

THE POLAROGRAPHY OF VANADIUM CHELATES WITH PYROCATECHOL AND PYROGALLOL

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Vanadate is quantitatively reduced to V(IV) when reacting with pyrocatechol or pyrogallol at pH ranging from 3 to 9. Blue complexes of V(IV), VOL and VOL_2^{2-} , formed with these reagents, are reduced to yellow complexes of V(III): VL^+ , $\text{VL}(\text{OH})_2^-$ and $\text{VL}_2(\text{OH})_3^{3-}$ on a mercury electrode; at pH ranging from 3.4 to 8.6 the $E_{1/2}$ of this reversible polarographic wave is equal to $-0.3-0.7$ V (s.c.e.). The values of complex stability constants of V(III) have been determined. The method of polarographic determination of vanadium in acetate buffer at ≈ 5.3 in the presence of 0.05M pyrocatechol has been suggested.

Potentiometric studies of V(IV) complexes with *o*-diphenols (denoted as H_2L), VOL and VOL_2 (ion charges omitted for the sake of simplicity) have been reported as well as reviewed in communication¹. Following ternary systems have been studied^{2,3} — V(V)-*o*-diphenol — large organic cation; ionic associates of univalent complex anions containing one or two diphenolic reagents can be extracted with dichloroethane. Both the reduction of V(V) to V(IV) and the formation of V(IV) complexes have been described in paper³. During photometric studies⁴ of complexes V(III) with tirone at pH ranging from 7 to 10 a complex 1 : 3 has been found, whose λ_{max} at 570 nm approaches that of the complexes V(IV). The latter are easily formed *via* oxidation of V(III) in the presence of atmospheric oxygen.

Polarographic behaviour of V(V), V(IV) and V(III), resp., has been studied in various media with oxygen-containing ligands. V(V) is, in these media, reduced⁵⁻⁷ to V(IV) on a mercury electrode at potential around 0 V (s.c.e.). Further reduction of V(IV) to V(II), and to V(III) (refs^{8,9}), resp., takes place in an irreversible wave⁵⁻⁷, ($E_{1/2}$ ranges from -0.6 to -1.4 V). A cathodic wave of the reduction of V(III) to V(II) has been observed^{9,10} at a considerably negative potential; it is reversible in an oxalate medium⁵ ($E_{1/2}$ equals to -1.32 V at pH = 4.5). Oscillopolarographic activity of V(V) has been observed in an ammonia buffer in the presence of *o*-diphenols¹¹. Polarographic behaviour of V(V) has been tentatively examined in 1M- NaClO_4 and 0.5M of pyrogallol solutions and two cathodic waves ($E_{1/2} = -0.13$ and 0.82 V, resp.) were observed¹². The waves have been assigned to the reduction of V(V) to V(IV), and of V(IV) to V(II), resp. The different stability of the V(III) and V(IV) complexes with pyrocatechol has been employed¹³ for the amperometric determination of V.

EXPERIMENTAL

Polarographic curves were registered on an OH-102 (Radelkis, Hungary) polarograph. A dropping mercury electrode with the flow rate 0.86 mg/s and a drop time 3.7 s in a 0.1M-KCl at a potential

of the saturated calomel electrode was used, the height of a reservoir being 42 cm. Kalousek vessel with a saturated calomel electrode (s.c.e.) was used. The measurements were carried out at $21 \pm 1^\circ\text{C}$. Polarograms were taken after c. five minutes bubbling of nitrogen through the solution. Each polarogram was registered twice; the values of $E_{1/2}$ differed by 4 mV at most. pH was measured on a PHK-1 pH-meter (CSSR) fitted with G 200C glass electrode and s.c.e. K-100 (Radiometer, Denmark). A phosphate buffer with pH 6.50 made by the same company was used for the calibration. To register the cathode-anode wave the reduction of V(IV) complexes was carried out using an electromagnetically stirred mercury cathode having c. 6 cm^2 surface; as a counter-electrode a s.c.e. electrode was employed connected with a cathode space by agar bridge. The constant potential of the mercury cathode was checked with a PHK-1 valve millivoltmeter using a third s.c.e. K-100 reference electrode. Shortly before and during the electrolysis the solution was bubbled through with nitrogen. Potentiostatic coulometry was carried out on an Electroscan 30 instrument (Beckman, USA). Vessels and electrodes used were the same as those used for the reduction of V(IV) complexes described above. The electromagnetic stirring, however, proved unsatisfactory because of considerable current fluctuations; additional efficient stirring was effected by bubbling of argon through the solution. Before the coulometric determination a preelectrolysis of a blank solution (*i.e.* of a solution containing all components except V(IV)) was made until the current decreased to almost a zero value.

A constant ionic strength, $I = 0.5$, in all measured solutions was ensured by the addition of KNO_3 , the constant pH value was maintained by means of buffers. Pyrocatechol and pyrogallol were purified by a distillation in a stream of nitrogen. Vanadyl sulphate was prepared by reduction of (di)vanadium pentoxide by sulphur dioxide in sulphuric acid medium; after concentration the crystals were filtered by suction, washed with alcohol and vacuum dried over silica gel. Other reagents used were of analytical purity (Lachema, Brno). Solutions of pyrocatechol and pyrogallol were freshly prepared in 0.01M-HNO_3 . Vanadium content in the stock solution 0.119M-VOSO_4 was determined both chelatometrically and manganometrically. Solution of V(V) was prepared from NH_4VO_3 and by boiling with an equivalent amount of NaOH it was transformed to sodium vanadate.

Electron-spin resonance (ESR) was registered on a ER-9 instrument (Zeiss, Jena, NDR).

RESULTS AND DISCUSSION

Polarographic reduction of V(IV) complexes with pyrocatechol and pyrogallol was investigated at pH ranging from 0 to 9, $c_M = 0.5\text{ mM}$ and $c_L = 6\text{--}400\text{ mM}$ (c_M and c_L being the total concentration of vanadium and phenolic reagent, c_T being the total concentration of the buffer, *i.e.* the sum of concentrations of conjugated acid and base). The waves due to V(IV) in 0.2M pyrocatechol and pyrogallol resp. in various buffers are shown in Figs 1 and 2 resp. They have the same form in the presence of both phenols, their values $E_{1/2}$ being also very close at the same pH and c_L . Only at $\text{pH} \gtrsim 7$ in pyrogallol medium the waves are distorted by oxidation products of pyrogallol whose reduction is seen in form of several waves within -700 and -1300 mV (Fig. 2, curve 3). In nitric acid medium at $\text{pH} = 0.6$ the solution of V(IV) with both diphenols is colourless and no reducing polarographic wave has been observed (compare with the results of potentiometric studies¹, where the complex formation was proved to begin from $\text{pH} \approx 2.5$). $E_{1/2}$ values of pyro-

catechol complexes of V(IV) in various buffers are given in the following table ($C_M = 0.5$ mM; $C_L = C_T = 200$ mM):

Buffer:	formate	acetate	pyridine	Tris + H ₂ L	TEA + H ₂ L	NH ₃ + H ₂ L	EA + H ₂ L
pH	3.5	5.6	5.5	7.7	7.5	8.7	8.7
$-E_{1/2}$, mV	330	620	580	720	720	720	720

H₂L denotes pyrocatechol, TEA triethanolamine, EA ethanolamine; only the wave in the first three buffers was fully developed and is suitable for analytical purposes; the $E_{1/2}$ value of the second wave was measured for the formate only (940 mV), the plateau of the wave is not, however, fully developed.

First Wave of V(IV)

In a formate buffer medium at pH 3.3–4.2 the first wave (at a more positive potential) is accompanied by a current maximum, which can be suppressed by addition of 0.005% of gelatine. Only in this medium the second reduction wave was observed (Fig. 1, curve 1). A "logarithmic analysis" of the first cathodic wave $E = f(\log i/i_D - i)$, where i denotes current at a potential E and i_D denotes limiting current, is a straight line dependence at $c_L = 20$ –400 mM, the slope being 62–82 mV for the

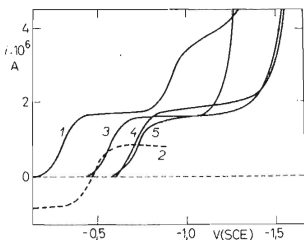


FIG. 1

Polarograms of V(IV) Pyrocatechol Complexes

$c_M = 0.5$ mM; $c_L = c_T = 200$ mM; 0.005% of gelatine. Buffer: 1 formate, pH 3.49; 2 pyridine, pH 5.04 (partly reduced on the mercury cathode); 3 pyridine, pH 5.48; 4 Tris, pH 7.82; 5 ammoniacal, pH 8.70.

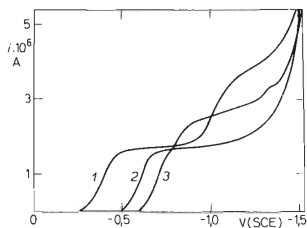


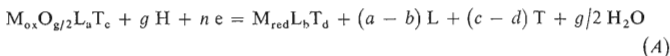
FIG. 2.

Polarograms of V(IV) Pyrogallol Complexes

$C_M = 0.5$ mM; $c_L = c_T = 200$ mM; 0.005% of gelatine. Buffer: 1 formate, pH 3.73; 2 acetate, pH 5.67; 3 Tris, pH 7.56.

formate buffer, 60–70 mV for the acetate and pyridine buffers and 60–65 mV for the phosphate and triethanolamine buffers. The slope of the value near 60 mV suggests that a reversible single electron electrode reduction, $V(IV) \rightarrow V(III)$, takes place. Higher values of the slope were found only at low c_L values (< 30 mM) and at $pH < 5$. The reversibility of the process $V(IV) \rightarrow V(III)$ in a pyrocatechol medium was observed even on anode–cathodic waves after a preceding electroreduction of $V(IV)$ solution on a mercury cathode at a potential corresponding to the limiting current of the first wave. In formate, acetate, pyridine and phosphate buffers, resp., only one anode–cathodic wave was seen without any indication of a plateau in the region of the zero current. The number of electrons n exchanged during the electrode reaction was also found out using potentiostatic coulometry at a potential corresponding to the limiting current of the first wave. During the electroreduction the dark blue colour of the solution changed to light yellow proportionally to the reduction of pyrocatechol $V(IV)$ complex to the $V(III)$ complex. The results of coulometric measurements gave $n = 1.01$ and 1.06 , resp., in formate and $n = 1.02$ and 1.06 , resp., in pyridine buffers; $E_{1/2}$ of the first wave in solutions of pyrocatechol and pyrogallol is not dependent on c_M within $c_M = 0.05 - 1.8$ mM. It follows that the $V(IV)$ complexes, whose mononuclear characteristics were examined potentiometrically¹, are also reduced to mononuclear $V(III)$ complexes. $E_{1/2}$ is changing with the change of the following characteristics: pH , c_L , c_T .

If the reversible electrode reaction (A) takes place, we can, on the basis of the relation (I), define¹⁴ the composition and stability constants of complexes participating in the electrode reaction. M_{ox} and M_{red} are the central atoms in their oxidized and reduced forms, resp., L and T the ligands, n number of electrons exchanged during the electrode reaction, $E_{1/2}$ and $E_{1/2}^0$ halfwave potentials of the $M_{ox} + ne \rightarrow M_{red}$ system in a complex medium and in absence of complexing agents, resp., β_{ox} and β_{red} are formation constants of the complex in oxidized and reduced forms, resp.:



$$(E_{1/2} - E_{1/2}^0) \frac{n}{0.06} = -\log \frac{\beta_{ox}}{\beta_{red}} - (a - b) \log |L| - (c - d) \log |T| - g \text{ pH} \quad (I)$$

The methods for determination of the parameters g , $(a - b)$, $(c - d)$, β_{ox} and β_{red} , resp., are discussed in the previous paper¹⁴.

The influence of c_L on $E_{1/2}$ of the first wave was studied while pH , c_T and c_M , resp., were kept constant. In the formate buffer at $pH 3.3 - 3.8$ and $c_L = 50 - 400$ mM, resp., $E_{1/2}$ is not dependent on c_L . It follows that the $V^{IV}OL$ complex found

potentiometrically in this medium¹ is reduced to the complex containing the same number of ligands L. The $E_{1/2} = f(\log c_L)$ dependence is linear with the slope $\Delta E_{1/2} : \Delta \log c_L = -60$ mV in the acetate buffer at pH ranging from 4.4 to 5.5 and $c_L = 50-400$ mM, and in the pyridine buffer at pH ranging from 4.4 to 5.5 and $c_L = 25-400$ mM, resp. The slope indicates that at $\text{pH} \approx 5$ the $\text{V}^{\text{IV}}\text{OL}_2^{2-}$ complex splits off a ligand during the reduction. The slope reaches the value of -30 mV in the phosphate buffer at $\text{pH} 6.48$ and $c_L = 60-400$ mM. $E_{1/2}$ is independent of c_L in phosphate buffer at $\text{pH} 7.14$, in the triethanol buffer at pH ranging from 6.9 to 7.7 and in the ammoniacal buffer at pH ranging from 8.3 to 8.6. The $\text{V}^{\text{IV}}\text{OL}_2^{2-}$ complex, present in these media, is reduced without the change of the number of coordinated particles L.

TABLE I

Approximate Values of Stability Constants of Pyrocatechol and Pyrogallol Chelates of V(III), V(IV), Their Ratios and Reagent Dissociation Constants, resp.

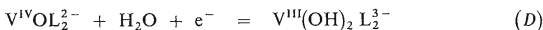
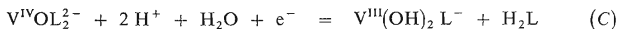
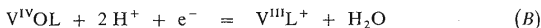
Expression for K	log K pyrocatechol	log K pyrogallol	Buffer
$\frac{[\text{V}^{\text{IV}}\text{OL}]/[\text{VO}^{2+}] \cdot [\text{L}^{2-}]}{[\text{V}^{\text{III}}\text{L}^+]/[\text{V}^{3+}] \cdot [\text{L}^{2-}]}$	- 0.6	- 0.3	formate
$\frac{[\text{V}^{\text{IV}}\text{OL}_2^{2-}]/[\text{VO}^{2+}] \cdot [\text{L}^{2-}]^2}{[\text{V}^{\text{III}}\text{L}(\text{OH})_2^-]/[\text{V}^{3+}] \cdot [\text{L}^{2-}] \cdot [\text{OH}^-]^2}$	-14.2	-13.7	acetate
	-14.0	-13.5	pyridine
$\frac{[\text{V}^{\text{IV}}\text{OL}_2^{2-}]/[\text{VO}^{2+}] \cdot [\text{L}^{2-}]^2}{[\text{V}^{\text{III}}\text{L}_2(\text{OH})_3^{3-}]/[\text{V}^{3+}] \cdot [\text{L}^{2-}]^2 \cdot [\text{OH}]^2}$	-14.3	-14.7	phosphate
	-14.0	-14.0	triethanolamine
	-14.2	-	ammonia
$[\text{V}^{\text{III}}\text{L}^+]/[\text{V}^{3+}] \cdot [\text{L}^{2-}]$	18.3	18.1	formate
$[\text{V}^{\text{III}}\text{L}(\text{OH})_2^-]/[\text{V}^{3+}] \cdot [\text{L}^{2-}] \cdot [\text{OH}^-]^2$	37.7	38.0	acetate
	37.5	37.8	pyridine
$[\text{V}^{\text{III}}\text{L}_2(\text{OH})_3^{3-}]/[\text{V}^{3+}] \cdot [\text{L}^{2-}]^2 \cdot [\text{OH}^-]^2$	47.8	49.0	phosphate
	47.5	48.6	triethanolamine
	47.7	-	ammonia
$[\text{V}^{\text{IV}}\text{OL}]/[\text{VO}^{2+}] \cdot [\text{L}^{2-}]$	17.7	17.8 ^a	ref. ¹
$[\text{V}^{\text{IV}}\text{OL}_2^{2-}]/[\text{VO}^{2+}] \cdot [\text{L}^{2-}]^2$	33.5	34.3 ^a	ref. ¹
$[\text{H}^+]^2 \cdot [\text{L}^{2-}]/[\text{H}_2\text{L}]$	23.1	23.0 ^a	ref. ¹

^a Dissociation constants of pyrogallol K_{a1} and K_{a3} were used, see¹.

The influence of acidity on $E_{1/2}$ of the first wave (with c_L , c_T and c_M being constant) is as follows: in formate medium at pH ranging from 3.4 to 3.8 and $c_L = 50-400$ mM the dependence $E_{1/2} = f(\text{pH})$ is a straight line with the slope equal to -120 mV, indicating the consumption of two protons during the electrode reaction. In acetate and pyridine media, resp., the slope indicates the consumption of 2.5 at $\text{pH} = 4.4$ to 4.9 and the consumption of 2.0 protons at pH ranging from 4.9 to 5.9, resp. $E_{1/2}$ is independent of the acidity of solutions at $\text{pH} 7.0-8.5$ in phosphate, ammoniacal and triethanolamine buffers, resp. It follows that $g = 0$ in these media.

The influence of c_T on $E_{1/2}$ of the first wave is small. In formate buffers the slope $\Delta E_{1/2}/\Delta \log c_T$ is equal to -10 mV in solutions with pyrocatechol and to -40 mV in solutions with pyrogallol at $c_T > 100$ mM, resp. At $\text{pH} > 5$ c_T does not influence the $E_{1/2}$ value. Potentiometric studies showed¹ that $\text{V}^{\text{IV}}\text{OL}_2^{2-}$ complex is saturated as for its coordination and that in solutions at $\text{pH} \geq 5$ it does not accept more ligands, neither L nor OH^- . It can thus be assumed that V(IV) complexes at pH approaching the value of 5 do not easily coordinate other ligands. Slopes of $\Delta E_{1/2} : \Delta \log c_T$ indicate rather higher affinity for V(III) complexes to formate ion than for V(IV) complexes. It seems that the formation of mixed complexes of both V(IV) and V(III) with formate and acetate takes place only in a small scale and can be pronounced only in solutions with low c_L (< 100 mM) and higher c_T (> 100 mM). For this reason mixed complexes of phenolic chelates of V(IV) and V(III) were not studied in detail in this work.

Parameters determined from the $E_{1/2}$ on c_L , pH and c_T dependencies, resp., indicate that the polarographic reduction of pyrocatechol and pyrogallol chelates of V(IV) can be described as follows: at $\text{pH} 3.4-4.2$ by reaction (B), at $\text{pH} 4.9-5.9$ by reaction (C), at $\text{pH} 7-8.5$ by reaction (D), resp.; at $\text{pH} 4.2-4.8$ by reactions (C) and (E) proceeding simultaneously:



Since the $E_{1/2}^0$ value is not polarographically accessible a tabulated¹⁵ value of the standard potential for the reaction ($\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- = \text{V}^{3+} + \text{H}_2\text{O}$) + 0.316 V (S.H.E.) was used in relationship (I) when calculating the $\beta_{\text{ox}}/\beta_{\text{red}}$ ratio. By using $E_{1/2}^0$ value for an ionic strength $I = 0$ and $E_{1/2}$ values measured at $I = 0.5$ an error is introduced into the calculation. Formation constants of the V(III) chelates were calculated from the values of $\beta_{\text{ox}}/\beta_{\text{red}}$ ratios and from the stability constants of V(IV)

chelates determined at $I = 0.1$ in work¹. Table I surveys stability constants of V(III) chelates and of V(IV) chelates, resp., and of their ratios together with the dissociation constants of reagents; the presented values are only approximation as the values used for their calculation were measured at various ionic strengths. Dissociation constants, K_{a1} and K_{a3} , resp., were used for the calculation of dissociation of pyrogallol to ligand $H_2L \rightarrow 2H^+ + L^{2-}$. This problem has already been discussed in work¹.

Second Wave of V(IV)

Relatively well developed second wave in the solutions of pyrocatechol and pyrogallol was observed only in formate buffer at $pH \approx 3.5$ (Fig. 1, curve 1). With the increasing pH the $E_{1/2}$ is shifted to more negative values; at $pH \gtrsim 5$ it coincides with the wave of the basic electrolyte. Linear dependence $E = f(\log i/i_d - i)$ with the slope equal to 85–95 mV indicates a slow electrode reaction in both phenolic reagents media. The number of electrons exchanged during the electrode reaction was not determined coulometrically because of an anomalous time dependence of the current. The height of the second wave is approximately the same as that of the first wave. It was thus deduced that this is due to the reduction of V(III) to V(II). The dependence of $E_{1/2}$ on $\log c_L$ indicates that the reduced form coordinates a lower number of ligands than V(III) and since V(III) complexes with one ligand L were found in this medium we assume that under this condition neither pyrocatechol nor pyrogallol is bonded to V(II). With regard to the imperfect reversibility of the electrode process the compound of V(II) formed during the electrode reduction cannot be precisely defined.

Reaction of V(V) with Pyrocatechol and Pyrogallol

Vanadate reacts with pyrocatechol and pyrogallol in weakly acidic and neutral solutions; blue complexes formed are of the same intensive colour as in the case of V(IV), and the polarographic waves have the same form and $E_{1/2}$ as those of V(IV) complexes. In pyrocatechol solutions where V(V) was present the cathode current preceding the first wave of V(IV) was observed, whose intensity was about 30% of the height of the first wave. If the V(IV) was added instead of the V(V), no current is observed till the start of the first wave due to V(IV) complex. The cathode current occurring before the first wave of V(IV) can be explained either by the electrode reduction of V(V) to V(IV) at more positive potentials or by the electrode reduction of pyrocatechol oxidation products formed during redox reaction of V(V) with the reagent. Oxidation products prepared by atmospheric oxidation of a pyrocatechol solution are reduced on the mercury electrode already at the potential when mercury dissolves. In pyrogallol solutions, to which V(V) was added, zero current was polaro-

graphically registered at first followed by the wave due to V(IV), then another wave appeared with $E_{1/2}$ corresponding to the reduction of pyrogallol oxidation products (-1.2 V at pH 5.8 in acetate buffer). Unless experiments are carried out in a perfectly inert medium the wave of pyrogallol oxidation products appears even during polarography of solutions prepared from V(IV) and pyrogallol; analogous solutions prepared from V(V) indicate considerably higher content of oxidation products during polarography. This clearly signifies that V(V) in solution is reduced to V(IV) by pyrogallol, and undoubtedly also by pyrocatechol; cathodic waves of V(IV) complexes and reagents oxidation products are then polarographically registered.

Photometric studies of pyrocatechol solutions with the addition of either V(V) or V(IV) in acetate medium at pH ≈ 5 , $c_L = 50$ mM, $c_M = 0.5$ and $c_T = 200$ mM have shown that these solutions have the same absorption in the region close to the absorption maximum of the V(IV) complex (λ_{\max} 580 nm). Absorption in 380–435 nm region effected by pyrocatechol oxidation products is substantially higher in solutions prepared from V(V). ESR spectra in acetate buffer at pH ≈ 5 , $c_L = 20$ mM, $c_M = 10$ mM were also taken. Diamagnetic V(V) does not give any signal; after the addition of pyrocatechol to the V(V) solution a signal, very similar to that due to pyrocatechol V(IV) complex, was seen. It follows from these results that V(V) is reduced to V(IV) by pyrocatechol and by other reagents with *o*-diphenolic group, resp.; this reduction was observed at pH ranging from 3 to 9. V(IV) formed during the reduction gives chelates with *o*-diphenols. Complexation of the reaction product favourably influences further redox reaction course so that the reduction to V(IV) is quantitative in the excess of *o*-diphenol.

Polarographic Determination of Vanadium in Pyrocatechol Solutions

Pyrocatechol complex of V(IV) gives a well developed polarographic cathodic wave in acetate or pyridine buffers at pH 5.3, $c_L = 50$ mM and $c_T = 200$ mM. $E_{1/2} = -0.53$ V, calibration curve is linear for $c_M = 0.07-2.4$ mM. At pH ranging from 5 to 6 and $c_L = 25-400$ mM the wave height is independent of pyrocatechol concentration and of solution acidity, resp. Under these conditions V(V) is reduced to V(IV) and V(III) oxidizes to V(IV) by air. It is thus possible to determine V(V), V(IV) and V(III), resp., as well as total vanadium content in V(V) + V(IV) and V(IV) + V(III) mixtures, resp.; calibration lines are identical for all mentioned oxidation forms of vanadium. Pyrogallol is a less suitable reagent for polarographic determination of vanadium the reason being its easy oxidation and the overlap of polarographic waves due to vanadium and pyrogallol oxidation products.

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REFERENCES

1. Zelinka J., Bartušek M.: This Journal 36, 2615 (1971).
2. Šnajderman S. Ja.: Ukr. Chim. Ž. 36, 426 (1970).
3. Šnajderman S. Ja., Prokofjeva G. N.: Ž. Anal. Chim. 25, 2368 (1970).
4. Cerkovnickaja I. A., Grigorjeva M. F., Loginova T. V.: *Primenenije Organičeskich Reaktivov v Analitičeskoj Chimii*, p. 83. Univ. Leningrad 1969.
5. Lingane J. J., Meites L.: J. Am. Chem. Soc. 69, 1021 (1947).
6. Breda E. J., Meites L., Reddy T. B., West P. W.: Anal. Chim. Acta 14, 390 (1956).
7. Baumgarten S., Cover R. E., Hofsass H., Karp S., Pinches P. B., Meites L.: Anal. Chim. Acta 20, 397 (1959).
8. De Sea M. A., Hume D. N., Glen H. C., De Ford D. D.: Z. Anal. Chem. 144, 200 (1955); Anal. Chem. 25, 983 (1953).
9. Lingane J. J., Meites L.: J. Am. Chem. Soc. 73, 2165 (1951).
10. Lingane J. J., Meites L.: J. Am. Chem. Soc. 70, 2525 (1948).
11. Matysik J.: Chem. zvesti 18, 407 (1964).
12. White M. C., Bard A.: Anal. Chem. 38, 61 (1966).
13. Cerkovnickaja I. A., Grigorjeva M. F.: *Metody Količestvennovo Opredelenija Elementov*. Univ. Leningrad 1964.
14. Zelinka J., Bartušek M., Okáč A.: This Journal 38, 2898 (1973).
15. Lingane J. J.: *Electroanalytical Chemistry*. Interscience, New York 1958.

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