
**POLAROGRAPHIC DETERMINATION OF ALKALINE EARTHS
WITH AZO DYES**

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

Magnesium and calcium can be determined in an alkaline medium as complexes with azo dyes by square-wave polarography on the dropping mercury electrode or by linear sweep voltammetry on the hanging mercury drop. The linear dependence of current on magnesium concentration in the presence of IREA magnezone is valid within half an order; in the presence of calcone in a wider range. The lower limit of determination is $2 \cdot 10^{-7} \text{ mol l}^{-1}$. The dependence of current on calcium concentration in the presence of calcion is linear within the interval of $5 \cdot 10^{-7}$ to $4 \cdot 10^{-6} \text{ mol l}^{-1}$ in the voltammetric determination with accumulation.

The complexity of polarographic reduction of alkaline earths is accounted for by the fact that it takes place in the region of negative potentials where the hydrogen ion discharge usually occurs and where the stability of the operation of the dropping mercury electrode is often disturbed.

Metal chelates with O, O¹ hydroxyazo dyes were introduced for polarographic determination of ions by Willard and Dean¹ who bound aluminium in the complex with mordant violet 5. Unfortunately, the use of the wide class of hydroxyazo dyes is limited due to their poor solubility.

Many metals form polarographically active complexes with solochrome violet RS in alkaline solutions. The waves of these complexes are shifted to potentials more negative than the wave of the dye. At pH 10 the magnesium complex is reduced at -0.88 V . The dependence of current on concentration remains linear within 1 to $7 \mu\text{g/ml}$. If calcium content in the sample does not exceed tenfold excess it does not interfere with magnesium determination since at pH 13 its complex with solochrome violet is polarographically inactive². Magnesium can be detected at pH 10 with the same ligand in presence of 100-fold calcium excess since the calcium complex is unstable under these conditions³. On the other hand, at pH 9.5 traces of calcium, magnesium, strontium and barium have been detected by inversion polarography with adsorptive accumulation of metals in complexes with solochrome violet on

the hanging mercury drop electrode. Accumulation at -0.8 V produced pronounced peaks on polarization curves in the region between -1.05 and -1.08 V. Each of the alkaline earths can be determined after separating all the others⁴.

High sensitivity of voltammetric determination (detection limit $2 \cdot 10^{-8} \text{ mol l}^{-1}$) has been achieved in the presence of ethylenediamine and cryochrome black T complexing with magnesium and calcium, due to adsorption processes on the electrode^{5,6}. Calcium can be also determined by the polarographic adsorption wave of its complex with thymolphthalexone⁷.

EXPERIMENTAL

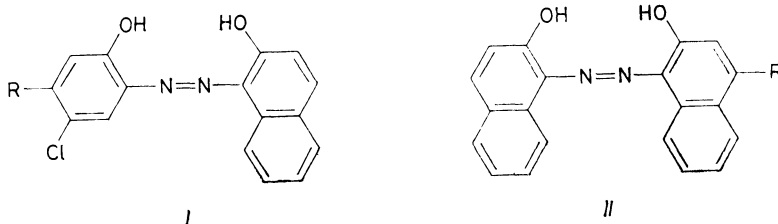
Equipment

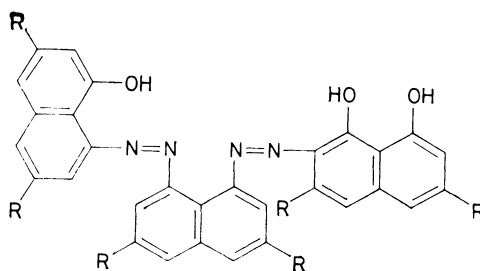
An oscilloscopic polarograph PO-5122 (U.S.S.R.) with a potential sweep in a single-pulse mode and a universal polarograph PU-1 (U.S.S.R.) in the mode of square-wave polarography were used. Measurements were carried out in a thermostated three-electrode cell at $(25 \pm 0.2)^\circ\text{C}$. A slowly dropping mercury electrode (droptime 8–10 s in 0.1 mol l^{-1} KCl with open circuit and with the height of mercury column 35 cm) and a hanging mercury drop electrode (model SMPE-1) were employed as indicator electrodes. The surface of the mercury drop was $2.06 \cdot 10^{-2} \text{ cm}^2$. The potentials were measured with reference to saturated calomel electrode (SCE). A platinum foil was used as the counter electrode in the three-electrode system. Oxygen was removed from solutions by argon or nitrogen.

Reagents

Solutions of $1 \cdot 10^{-3} \text{ mol l}^{-1}$ calcium and magnesium were prepared from calcinated CaO and MgO, "c.p." grade, by dissolving weighed samples in dilute HCl. The concentration of solutions was measured complexometrically. Azo dyes were purified by recrystallization from ethanol. Magneson IREA (*I*) ($(2-5) \cdot 10^{-3} \text{ mol l}^{-1}$) was obtained by dissolving the weighed sample of the substance in the mixture methanol-acetone-water in proportion 2 : 5 : 3 while heating on a water bath. Calcione (*II*) ($5 \cdot 10^{-3} \text{ mol l}^{-1}$) was obtained by dissolving the sample in water under moderate heating, calcion (*III*) ($1.25 \cdot 10^{-4} \text{ mol l}^{-1}$) by dissolving the sample in water.

Solutions of hydrochloric acid and ammonium hydroxide were purified by isothermal distillation. All solutions were made from bidistilled water.





III

R = SO₃H

Procedure

Magnesium: 0.5 ml of $1 \cdot 10^{-3} \text{ mol l}^{-1}$ magnesium solution was introduced into a 10 ml volumetric flask, then 1.5 ml of the solution of *I* or *II* were added and an ammonium–ammonia buffer was used to fill the flask to the mark. The reaction of magnesium with both *I* and *II* occurs instantly already at room temperature. The resulting solution was placed into the polarographic cell and deaerated by argon for 10 min. The oscilloscopic polarograph operated in the following setting: initial potential $E_{in} 0 \text{ V}$; scan rate $v - 0.5 \text{ V/s}$; relative sensitivity (R.S.) $10 \mu\text{A}/20$ scale divisions or the screen height. The square wave polarograph operated in the following setting: R.S. 0.25×10 , $M_x 100 \times 2$, $M_y 1 \times 1$; square wave amplitude $A_N 20 \text{ mV}$, $v - 2 \text{ mV/s}$. Peaks at $E_1 = -0.48 \text{ V}$ mark the reduction of *I* and at $E_2 = -0.63 \text{ V}$ the reduction of magnesium from the complex with *I* and their heights correspond to the contents of *I* and magnesium in the sample, as determined by calibration curves. The main peak of *II* appears at -0.57 V , the following peak, 15–20 times smaller, at -0.76 V . The peak of the magnesium–*II* complex appears at -0.88 V and increases in proportion with the magnesium concentration near the second peak of *II*.

Calcium: 5 ml of $10 \text{ mol l}^{-1} \text{ NH}_4\text{OH}$, 1 ml of $0.1 \text{ mol l}^{-1} \text{ KOH}$, 1 ml of $1.25 \cdot 10^{-4} \text{ mol l}^{-1}$ solution of *III* and $(0.25-2) \text{ ml}$ of $5 \cdot 10^{-5} \text{ mol l}^{-1}$ calcium solution were introduced into a 25 ml volumetric flask. Water was added to fill the flask to the mark. The solution was transferred into the polarographic cell and oxygen was removed from it by bubbling nitrogen for 10 min. Operational setting: $v - 0.25 \text{ V/s}$, potential of accumulation $E_{acc} = -0.30 \text{ V}$, accumulation time $t_{acc} = 60 \text{ s}$. Accumulation was started 20 s after the end of deaeration and carried out without stirring the solution. The potential of reduction of the complex was near that of the reduction of the dyes, i.e. at -0.64 V .

RESULTS AND DISCUSSION

Polarographic Behaviour of IREA Magnezone and of its Magnesium Complex

Polarographic characteristics of *I* and the corresponding peak morphology depend on pH. With an increase of pH the peak potential shifts to the region of electrocapillary zero and the peak shape changes to an elongated isosceles triangle. This is characteristic of reduction of a depolarizer adsorbed at the electrode, and the oc-

currence of adsorption is confirmed by the results of electrocapillary measurements (Fig. 1, A, B). A complex study of the reduction of *I* in aqueous-methanolic medium in ammonium-ammonia supporting electrolyte of pH 9.5–10 proved that the process is irreversible and accompanied by adsorption⁸.

At $\text{pH} \geq 10$ the complex of magnesium with *I* is reduced in the potential region near the reduction of *I* alone which strongly limits the possibilities of magnesium determination. On the one hand an excess of the ligand is necessary in order to obtain the wave of the complex; the greater the excess, the higher the wave. However, on the other hand, the increase of concentration of *I* makes the magnesium wave indistinct and unsuitable for determination. The linear relationship between

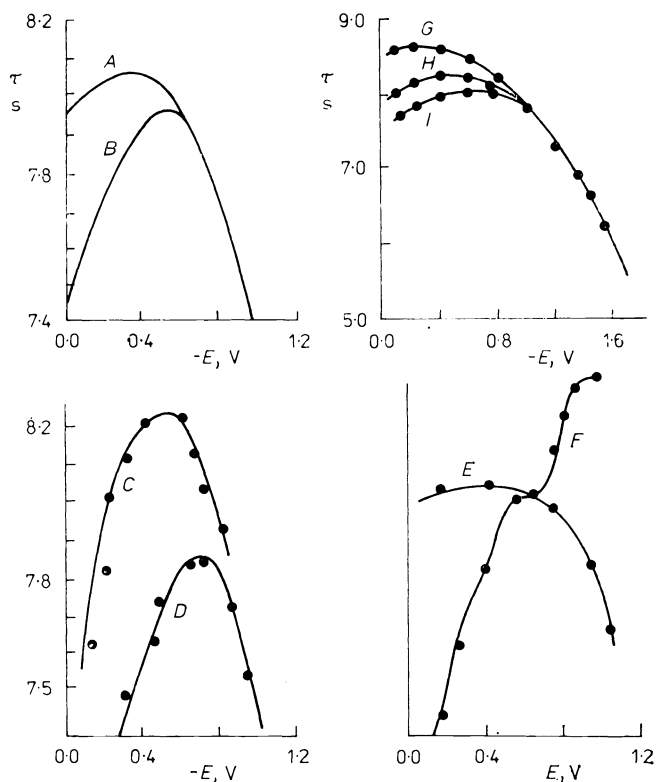


FIG. 1

Drop time vs potential in solutions: A $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ in CH_3OH ; B as A + $4 \cdot 10^{-4} \text{ mol l}^{-1}$ *I*; C $0.05 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$; D as C + $2 \cdot 10^{-4} \text{ mol l}^{-1}$ *II* + $5 \cdot 10^{-5} \text{ mol l}^{-1} \text{ Mg}^{2+}$; E $\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1 : 1$, pH 12.6; F as E + $2 \cdot 10^{-4} \text{ mol l}^{-1}$ *II* + $5 \cdot 10^{-5} \text{ mol l}^{-1} \text{ Mg}^{2+}$; G $2 \text{ mol l}^{-1} \text{ NH}_4\text{OH} + 4 \cdot 10^{-3} \text{ mol l}^{-1} \text{ KOH}$ (pH 12.3); H as G + $4 \cdot 10^{-5} \text{ mol l}^{-1}$ *III*; I as H + $4 \cdot 10^{-5} \text{ mol l}^{-1} \text{ Ca}^{2+}$

the value of the current due to reduction of magnesium and the concentration of magnesium holds within an interval of half an order. Besides, the complex of *I* with magnesium has a low stability. An important feature of *I* is its extractability by 1-butanol from solutions of $\text{pH} \geq 10$. A similar ability characterizes also the magnesium complex of *I* (ref.⁹). This property and the possibility to apply polarography to the extract were used to detect magnesium in alloys of non-ferrous metals (Table I).

Polarographic Behaviour of Calcone and of its Complex with Magnesium

The potential of the main wave of *II* (further on only this wave is mentioned) depends on pH of the medium and on concentration of the depolarizer itself. An increase of pH shifts the peak potential in the negative direction. This is due to the proton-consuming reduction of azo compounds. An increase of depolarizer concentration shifts the peak towards positive potentials. The current of reduction of *II* increases linearly with concentration up to a definite level. At concentrations exceeding $5 \cdot 10^{-4} \text{ mol l}^{-1}$ the calibration curve attains a limit indicating adsorption of *II* on the electrode.

The polarographic behaviour of *II* has been studied in both aqueous and mixed medium. Table II shows the data from the study of diagnostic criteria of the reduction of *II* in aqueous solution and in presence of dimethylformamide (DMF). In voltammetry in presence of DMF the peak morphology changes: when $I_{0.2}$ symbolizes the current at potential more negative by 0.2 V than at the peak and I_c is the (cathodic) current at the peak, the ratio $I_c/I_{0.2}$ increases what indicates a relative decrease of the effect of adsorption in the reduction process. Besides, the pressure of the mercury column over the tip of the capillary hampers the reduction current which is possibly related with the depolarizer solvation that impedes discharging. The change of initial potential does not change the value of the reduction current of *II*. In both pure aqueous and DMF containing medium the cyclic voltammogram features a great potential difference ΔE_{ac} between the cathodic and anodic peaks and also a high value of the I_c/I_a ratio what indicates an irreversibility of the reduction process. Compound *II* is adsorbed on the mercury surface, as is indicated also by the results of electrocapillary measurements (Fig. 1, C, D). The figure shows the electrocapillary maximum shifted to negative potentials and a considerable lowering of surface tension of mercury in the presence of *II*. The conspicuous increase of drop-time marked at $E < -0.8 \text{ V}$ is connected with the process of electroreduction of *II*: the second wave of *II* and the discharge of magnesium ions occurs in this potential region.

The current due to reduction of the complex of magnesium with *II* at constant concentration of *II* changes proportionally to the magnesium concentration. However, the proportionality holds only as long as the concentration of *II* exceeds that

of magnesium. The current of reduction of magnesium increases with the concentration of *II*. In the complex with *II* magnesium can be determined in a considerably wide range of concentrations. The lower limit of determination by means of square-wave polarography is $2 \cdot 10^{-7} \text{ mol l}^{-1}$.

The relationship $I_{\text{Mg}} = f(c_{\text{II}})$ remains valid even when the main wave of *II* reaches its limit at the calibration graph. Figure 1 shows electrocapillary curves of mercury in different solutions in presence and in absence of *II* and magnesium. As can be seen, in the supporting electrolyte of Na_2SO_4 compound *II* causes lowering of the surface tension and addition of magnesium to the solution causes no change in drop-time. No changes are also found on electrocapillary curves of the supporting electrolyte of $\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1 : 1$ in the presence of magnesium.

TABLE I

Magnesium detection in alloys; $n = 5$, $r = 0.95$

Alloy composition ^a	Detected \bar{X} , %	S_r	$(\bar{X} \pm \delta)$, %
Mn 4.02; Cu 0.67; Si 0.61; Fe 1.03; Sb 0.0014 Mg 0.103	0.091	0.112	0.091 ± 0.025

^a Alloy 2,5 S.S.S. 2553—83 is certified.

TABLE II

Polarographic characteristics of calcone and of its complex with magnesium

No	Conc. 10^4 mol l^{-1}		Solution composition	$\frac{\log I}{\log E}$	$\frac{\log I}{\log \tau_z}$	$\frac{I_c}{I_a}$	ΔE_{ac}	$\frac{\log I}{\log H_{\text{Hg}}}$
	<i>II</i>	Mg						
I	1	—	$\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1 : 1$	0.65	0.86	12	0.122	0.5
II	1	—	I + 10 vol. % DMF	0.5	0.6	2.4	0.173	0.4
III	4	1	$\text{NH}_4\text{OH} : \text{H}_2\text{O} = 1 : 1$	0.5	0.4	4.0	0.155	0.9

I Polarographic current; *E* potential of the working electrode τ_z drop-time at the potential of zero charge; I_c , I_a voltammetric peak currents; ΔE_{ac} potential difference between the anodic and cathodic peak in voltammetry; H_{Hg} height of the column of mercury

The changes of the initial potential has no effect upon the value of the reduction current of the complex. The value of the ratio $\log I/\log H_{Hg}$ indicates adsorption. If we increase in square-wave polarography the pulse-delay time before drop detachment, i.e., create conditions more favourable for adsorption, the rate coefficient increases to 0.64. Thus the cause of the high sensitivity of magnesium determination in the complex with calcone is the adsorption of the complex; consequently, its reduction occurs from adsorbed state.

The main wave of *II* decreases in the presence of calcium as a result of complex formation. However, we failed to detect the calcium wave even at high concentration of calcium; its 100-fold excess does not impede the polarographic determination of magnesium. Strontium does not interact with calcone and even its 100-fold excess does not interfere with the magnesium determination. Barium interacting with *II* is liable to detection only at its great excess and the wave of the barium complex is of low sensitivity. A 10-fold excess of barium does not impede the determination of magnesium.

Polarographic Behaviour of Calcion and of its Complex with Calcium

In the supporting electrolyte of $2 \text{ mol l}^{-1} \text{ NH}_4\text{OH} + 1 \cdot 10^{-3} \text{ mol l}^{-1} \text{ KOH}$ (pH 12.3), compound *III* yields one four-electron reduction peak of the shape of an isosceles triangle. In the presence of calcium ions the height of this peak increases with the increase of calcium content in the solution. The value of the current due to reduction of *III* and also of its complexes with calcium depends on the potential of accumulation (E_{acc}). A shift of E_{acc} towards positive potentials causes an increase of the peak current. In all experiments E_{acc} and v were kept constant and equal to -0.30 V and -0.25 V/s , respectively.

The effect of pH in the interval of 9.0–13.5 on the reduction current of complexes calcium–*III* is such that with the increase of pH the current reaches its maximum at pH 12.0–12.4. Figure 2 shows the dependence of I_p of calcium *III* complexes on the time of accumulation for different concentrations of complexes in the solution.

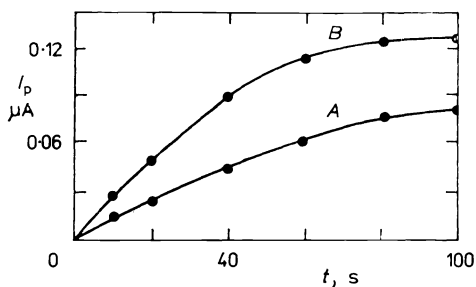


FIG. 2
 I_p of calcium–*III* complexes vs. accumulation time; $C_{Ca} = C_{III}$. A $C = 0.6 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$; B $C = 1 \cdot 10^{-6} \text{ mol l}^{-1}$

The current increases with the accumulation time and reaches a saturation limit. For more concentrated solutions the limit is reached faster.

The given relationships indicate that the discharge of calcium complexes with calcium is accompanied by the depolarizer adsorption on the electrode surface. The rate coefficient is 0.78. The dependence of drop-time on electrode potential (Fig. 1, H, I) indicates a stronger adsorption of calcium complexes in comparison with calcium adsorption, compound *III* as well as its complexes with calcium being adsorbed mainly on the positive branch of the electrocapillary curves.

After having measured the quantity of electricity (Q) for different concentrations of complexes we determined the maximal surface concentration of complexes on the electrode $\Gamma_{\max} = 4.79 \cdot 10^{-11} \text{ mol cm}^{-2}$. From the ratio of Q values for different concentrations of complexes in the solution to Q_{\max} ($0.381 \cdot 10^{-6} \text{ C}$) the degree of electrode coverage by the adsorbed particles was determined¹⁰.

A linear dependence was obtained when plotting $\log Q/(1 - Q) \cdot c$ versus Q . In compliance with Frumkin adsorption isotherm the slope of this straight line is $\text{tg } \alpha = 2\gamma$ where γ is the attraction constant characterizing interaction between the particles adsorbed on the electrode surface. The slope of the straight line is 0.64 which corresponds to $\gamma = 0.74$. A positive γ indicates mutual attraction of particles on the electrode surface. The intersection point of the straight line with the ordinate determines the value of B , the constant of adsorption equilibrium in the equation of Frumkin adsorption isotherm; B is equal to $1.12 \cdot 10^5 \text{ l mol}^{-1}$. The fraction of electrode surface occupied by one complex particle has been computed as $S = 347 \text{ \AA}^2$ (the value calculated on basis of model is 356 \AA^2).

The reduction on the electrode of complexes of calcium with *III* is irreversible. With the increase of scan rate E_p shifts towards negative potentials. The value of αn_x was computed from the slope of the straight line in coordinates $E_p - \log E$ as 1.43 and it was also computed from the width of the half-peak from the equation $\alpha n_x = 0.0625/\Delta$, where Δ is the half-peak width in volts – in this case the value of αn_x was found as 1.76.

TABLE III

Determination of calcium by means of the adsorption wave of calcium-*III* complexes; n 5; r 0.95

Water sample (100 ml)	$C_{\text{Ca}} \cdot 10^6$ mol l^{-1}	S_r	$\pm \delta$ mol l^{-1}
Water from still	1.1	0.091	0.009
Water from still of "Purator" type	0.4	0.113	0.014

The form and height of the reduction wave of the calcium-III complexes depend upon the nature of the supporting electrolyte. The most suitable supporting electrolyte for quantitative determination of calcium in the presence of III is a 2 mol l^{-1} solution of $\text{NH}_4\text{OH} + 4 \cdot 10^{-3} \text{ mol l}^{-1} \text{ KOH}$ (pH 12.3). In the presence of NH_4^+ ions the voltammogram gives a more pronounced peak, higher than in solutions of K^+ or Na^+ salts.

At low concentrations of calcium the current due to reduction of the complex is small in comparison with the reduction current of III what causes poor reproducibility of results. This drawback can be overcome by introducing a surfactant — sodium dodecylsulfate — which has a small effect on the complex adsorption but reduces considerably the adsorption of III. In this way the reproducibility of calcium determination is improved.

A linear dependence of I_p on calcium concentration holds from $5 \cdot 10^{-7}$ to $4 \cdot 10^{-6} \text{ mol l}^{-1}$. Magnesium interferes with the determination of calcium in these conditions. Calcium can be bound in a complex with GEDTA (bis-glycol ether of ethylenediamine-tetraacetic acid). The complexes of calcium and magnesium with GEDTA are of different stability (pK for the calcium complex is 10.97 and for magnesium 5.21). This can be utilized in masking calcium when determining magnesium. Using the difference of currents due to reduction of complexes in the presence and in the absence of GEDTA one can determine both elements. The determination of calcium is not hampered by strontium or barium in proportions Ca : Sr = 1 : 10 and Ca : Ba = 1 : 20.

Determination of Calcium in Distilled Water

An amount of 100 ml of the water to be analysed are put in a beaker and evaporated to dryness. The dry residue is dissolved in 2–3 ml of $1 \text{ mol l}^{-1} \text{ HCl}$ and again evaporated to dryness. Bidistilled water (4–5 ml) is added to the dry residue and the solution is transferred into a 25 ml volumetric flask. An amount of 5.7 ml of $8.8 \text{ mol l}^{-1} \text{ NH}_4\text{OH}$ solution, 0.5 ml of $0.2 \text{ mol l}^{-1} \text{ KOH}$ solution, 0.25 ml of $5 \cdot 10^{-5} \text{ mol l}^{-1}$ solution of III, 0.5 ml of $2.5 \cdot 10^{-3} \text{ mol l}^{-1}$ solution of sodium dodecylsulfate are added into it and the flask is then filled to the mark by bidistilled water. The solution thus obtained is transferred into the polarographic cell and oxygen is removed. The voltammogram of calcium-III complex is recorded in the way described above. The calcium content is determined by means of a calibration curve. The results of calcium determination are given in Table III.

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