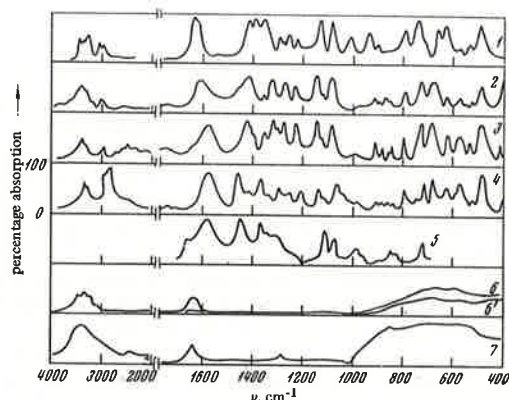


spectrum 7), and niobium pentoxide (Figure, spectrum 6'). In niobium hydroxide no bands for Nb-OH deformation vibrations in the 900-1100 cm^{-1} region were found although it has been stated that in the process of ageing niobium hydroxide bands appear at 1160 and 1080 cm^{-1} .¹⁰ Evidently the ageing conditions used by Hughes¹⁰ were different. The niobium hydroxide obtained, according to the classification of hydroxides¹¹⁻¹³, is hydrated niobium pentoxide with strong hydrogen bonds, as indicated by bands for stretching and deformation vibrations of water at 3400 and 1640 cm^{-1} and the corresponding bands in deuterated niobium hydroxide at 2400 and 1290 cm^{-1} . The wide band at 900-400 cm^{-1} is accounted for by niobium-oxygen groupings.



Infrared spectra of niobium and sodium tartrates and niobium pentoxide and hydroxide: 1) sodium tartrate, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$; 2) complex I (pH 4.5); 3) complex I partially deuterated; 4) complex II (pH 6.5); 5) complex III (pH 6.5); 6) niobium hydroxide; 6') niobium pentoxide; 7) deuterated niobium hydroxide. Spectra 6 and 7 were recorded using a paste with liquid paraffin, the others using KBr tablets.

The band at 670 cm^{-1} , which is absent from sodium tartrate and other tartrates, can be assigned to vibrations of the niobium-oxygen octahedron¹⁴.

Thus the sparingly soluble niobium tartrate formed at pH 4.5 has the formula $\text{Nb}(\text{OH})_5\text{OOC}-\text{CHOH}-\text{CHOH}-\text{COO}$. It is impossible to judge from the infrared spectra whether multinuclear complexes are formed and therefore the above formula does not reflect all the features of the structure.

Complex II, $\text{Nb}(\text{OH})_3(\text{C}_4\text{H}_4\text{O}_6)_2$, isolated at pH 6.5

As a pH change might cause a change in the state of the niobium and the structure of complexes I and II, which have the same composition, might be different, the infrared spectrum of complex II was recorded (Figure, spectrum 4). It is similar to that of complex I isolated at pH 4.5.

Complex III, $\text{NaNb}(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_6)_2$, isolated at pH 6.5

In the infrared spectrum of this compound (Figure, spectrum 5) there are again no bands above 1670 cm^{-1} and this shows that free carboxyl groups are absent. Although the form of the bands in the 1250-1350 cm^{-1} region changes as compared with sodium tartrate, these bands are so poorly resolved that it is difficult to say whether there are coordinately bound hydroxo-groups in this compound. An attempt was made to obtain the infrared spectra of aqueous solutions of niobium tartrates. However it was not possible to detect any bands in the 1200-1350 cm^{-1} region owing to the impossibility of obtaining a sufficiently high concentration of niobium in solution. Although the spectrum of complex III was not recorded in the lithium fluoride prism region, the presence of a band at 1000 cm^{-1} comparable in intensity with that in sodium tartrate shows that free hydroxo-groups of the tartrate are present. The presence of only two bands in the 1080-1140 cm^{-1} region indicates that there are no coordinated tartrate hydroxo-groups. An Nb=O band was not found.

The structure of complex III can thus be represented $\text{NaNb}(\text{OH})_2(\text{OOC}-\text{CHOH}-\text{CHOH}-\text{COO})_2$.

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Use of Polarography in the Determination of the Instability Constants of Complexonates of Readily Hydrolyzable Elements

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A polarographic method for the determination of the instability constants of complexonates is proposed, which does not have limitations in relation to acidity or the ratio of the reacting metals and EDTA.

Values of the concentration instability constants of complexonates have been determined: for bismuth $K = 10^{-27.9}$, for zirconium $K = 10^{-28.4}$, for niobium $K = 10^{-40.0}$.

The polarographic method has found wide application for determining the instability constants of many complexes.¹⁻⁶ According to Shlefer's handbook¹, use of the polarographic method is possible only under conditions when the complexonates have the simplest composition, with a metal: EDTA ratio of 1:1; the initial concentrations of the reacting metals and complexone are equivalent to one another, that is, $cM_1 = cM_2 = c\text{EDTA}$; the investigation can be made only in a range of solution acidities, close to pH 4.

According to the second and third conditions, polarography cannot be applied to the determination of the instability constants of complexonates of readily hydrolysable elements, which often need an acid medium and a large excess of the ligand for their formation.

Theoretical consideration of the reaction of EDTA with several metals present in solution, M_1, M_2, \dots, M_n ,^{7,8} and employing the concept of "conditional instability constants"⁹, the yield of the complex⁷ or the fraction of the complex² "B" show that the equilibrium conditions can be represented by the following equations:

$$A = B + \frac{K}{c} \frac{B}{1-B} \quad (1)$$

for systems consisting of one metal and EDTA (single-metal systems)⁷ and

$$A_1 = B_1 + \frac{c_2/c_1}{1 + \frac{K_2}{K_1} \frac{1-B_1}{B_1}} + \frac{K_1}{c_1} \frac{B_1}{1-B_1}, \quad (2)$$

$$A_2 = c_2/c_1 B_2 + \frac{1}{1 + \frac{K_1}{K_2} \frac{1-B_2}{B_2}} + \frac{K_2}{c_1} \frac{B_2}{1-B_2}, \quad (2a)$$

for systems consisting of two metals M_1 and M_2 and EDTA (two-metal system)⁸, where A is the relative concentration of complexone, $A = c_Y/c_1$; B is the yield (fraction) of a complex, equal to the ratio $B_1 = [M_1Y]/c_1$ and $B_2 = [M_2Y]/c_2$; c_1 and c_2 are the initial concentrations of the metals M_1 and M_2 in the solution, the volume of which is assumed to be unchanged; K_1 and K_2 are the conditional instability constants of the complexonates M_1U and M_2U ; and c_Y is the initial EDTA concentration.

From Eqns. (1) and (2), clearly on being given any values of the relative concentration of EDTA (A), any ratio of the metal concentrations (c_2/c_1), and the yield B determined experimentally for any value of the acidity, a value of the conditional instability constant for a single-metal system or a ratio of the instability constants of the metal complexonates (K_2/K_1) for a two-metal system can be calculated; if one of the constants is known, the second can be determined.

Determination of the value of the yield B for given experimental conditions by a polarographic method extends the range of use of polarography for finding instability constants compared with that of the methods described in the literature.

The value of the conditional instability constant K is connected with the value of the concentration or stoichiometric instability constant K_{instab} by the equation:

$$K_{\text{instab}} = K \Phi \cdot F, \quad (3)$$

where Φ and F are the complexability functions¹⁰ or hydrogen functions of EDTA and the metal respectively⁸.

Having calculated the hydrogen functions of EDTA (Φ) and of the metal (F) from the dissociation constants, it is then easy to calculate the value of the concentration instability constant.

The use of Eqns. (1) and (2) is a more general solution to the problem of calculating the instability constants of complexonates.

The method of determining the yield of a complex from polarographic results (direct and indicator) and of calculating the instability constants with Eqns. (1) and (2) was checked for elements of which the instability constants are given in the handbooks⁶: values of pK for cadmium, aluminium, manganese, and zinc have been determined.

This was done by mixing the appropriate amounts of the initial solutions of the metals and EDTA, establishing the acidity necessary to prevent hydrolysis, and then bringing the solutions to a definite volume. Part of the solutions was transferred to an electrolysis vessel and, after nitrogen had been bubbled through the solution, it was polarographed at appropriate limits of polarisation potential: cadmium, from -0.2 to -1.2 V; bismuth from +0.5 to -0.5 V; niobium, from -0.4 to -0.8 V (s.c.e.).

Direct Method

Cadmium in hydrochloric acid medium (pH 2.7) is reduced at a mercury dropping electrode at $E_1 = -0.6$ V. On adding EDTA in hydrochloric acid solution the cadmium bonds the metal in a complexonate and on the polarogram a second wave appears with $E_2 = -0.9$ V, corresponding to the reduction of the cadmium complexonate. With increase in the EDTA concentration in the solution, the heights of the first and second waves (i and I) respectively decrease and increase. Starting from a certain excess of EDTA, dependent on the conditional instability constant of the complexonate, the height of the complexonate wave I reaches its maximal value I_{max} : the cadmium ions have all passed into the complexonate. The ratio of the heights of the waves $I/I_{\text{max}} = B$ determines the yield of complex under the given conditions.

Table 1. Yield of cadmium complexonate as a function of the EDTA concentration and calculation of the concentration instability constant. Cadmium concentration 8.9×10^{-4} M, pH 2.7 ($I = 0.2-0.4$; KCl).

| EDTA concn., c_Y | $A = \frac{c_Y}{c}$ | $B = \frac{I}{I_{\text{max}}}$ | $K = (A-B) \frac{1-B}{B}$ | $K_{\text{instab}} \frac{K}{\Phi \cdot F}$ |
|----------------------|---------------------|--------------------------------|---------------------------|--|
| $3.8 \cdot 10^{-4}$ | 0.4 | 0.42 | $9.85 \cdot 10^{-6}$ | $10^{-16.30}$ |
| $5.76 \cdot 10^{-4}$ | 0.6 | 0.65 | $3.5 \cdot 10^{-6}$ | $10^{-16.0}$ |
| $7.65 \cdot 10^{-4}$ | 0.8 | 0.74 | $4.6 \cdot 10^{-6}$ | $10^{-16.7}$ |
| $1.32 \cdot 10^{-3}$ | 0.5 | 0.90 | $5.7 \cdot 10^{-6}$ | $10^{-15.6}$ |
| $2.15 \cdot 10^{-3}$ | 2.4 | 0.96 | $5.4 \cdot 10^{-6}$ | $10^{-16.0}$ |
| $3.8 \cdot 10^{-3}$ | 20.0 | 0.99 | — | — |
| $3.6 \cdot 10^{-2}$ | 40.0 | 0.99 | — | — |
| $5.4 \cdot 10^{-2}$ | 60.0 | 0.99 | — | — |
| Mean | | | $3.4 \cdot 10^{-6}$ | $10^{-16.01}$ |

Table 1 and Figs. 1 and 2a give the results of the polarographic measurements and of the calculation of the conventional instability constants of cadmium complexonate. The value of K_H was calculated by Eqn. (3) in which $\Phi = 10^{11.30}$ for pH 2.7,⁷ and $F = 1$, since at pH 2.7 the cadmium ions are not hydrolysed.

As Table 1 shows, the value found for the concentration instability constant of cadmium complexonate is $K_{\text{instab}} = 10^{-16.01}$, which agrees satisfactorily with the published⁶ value of $10^{-16.46}$.

Bismuth is an easily hydrolysable element and therefore was investigated in strongly acid solution under conditions for which the polarographic method of determining instability constants has not been used.

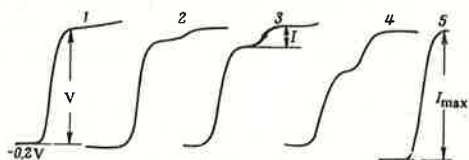


Figure 1. Polarograms of cadmium in the presence of various amounts of EDTA. Cadmium concentration 8.9×10^{-4} M; EDTA concentration (M): 1) 0.0; 2) 0.95×10^{-4} ; 3) 1.9×10^{-4} ; 4) 3.7×10^{-4} ; 5) 5.0×10^{-4} .

In nitric acid solution at an acidity of 1.78 M (pH 0.25) distinct, readily reproducible waves for the reduction of bismuth at $E_1 = 0.05$ V are obtained; in the presence of EDTA a second wave with $E_1 = -0.27$ V appear. Table 2 gives the results of the determination of the yield of bismuth complexonate as a function of the EDTA concentration. On the basis of the results, we have plotted the relation $B = f(A)$ (Fig. 2b) and calculated the conditional instability constant $K = 7.58 \times 10^{-4}$.

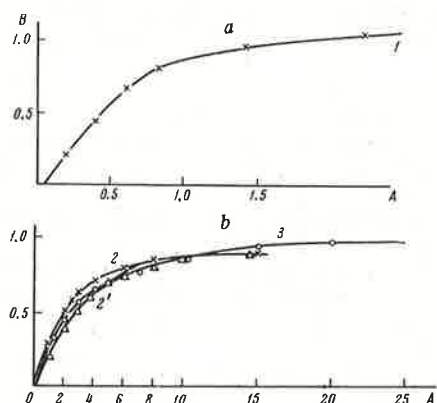


Figure 2. Variation of the yield of cadmium(1), bismuth(2), and niobium(3) complexonates with the relative concentration of EDTA in the solution. 2') Yield of bismuth complexonate in the presence of zirconium.

The value of the concentration instability constant of bismuth complexonate, $K_{\text{instab}} = 10^{-27.93}$, calculated similarly to cadmium, agrees well with the published value¹¹ of $10^{-27.94}$.

The agreement between the values for the instability constants for cadmium and bismuth with the published values confirmed the correctness of the proposed method

and showed the possibility of using it for the determination of unknown constants, such as that of niobium complexonate in particular.

Niobium. The optimal conditions for the formation of niobium complexonate and information about its composition¹² were used by us to calculate its instability constant. The experimental results are given in Fig. 2b and Table 3. The mean value of the conditional instability constant of the niobium complexonate is: $K = 2.84 \times 10^{-4}$, and the concentration instability constant calculated by Eqn. (3) is $K_{\text{instab}} = 10^{-39.4}$; the values of Φ and F were taken from Refs. 7 and 12 respectively. The value found for the constants agrees satisfactorily with the value $K_{\text{instab}} = 10^{-40}$ which we found earlier¹² from the relation $B = f(\text{pH})$.

Table 2. Yield of bismuth complexonate as a function of the EDTA concentration and calculation of the conditional instability constant of bismuth complexonate. Bismuth concentration 4.8×10^{-4} M ($I = 3.6$; HNO_3).

| EDTA concn., c_Y | $A = \frac{c_Y}{c_{\text{Bi}}}$ | $B = \frac{I}{I_{\text{max}}}$ | $10^4 K$ |
|----------------------|---------------------------------|--------------------------------|----------|
| $1.4 \cdot 10^{-4}$ | 0.3 | 0.10 | 8.8 |
| $2.8 \cdot 10^{-4}$ | 0.6 | 0.20 | 7.7 |
| $4.8 \cdot 10^{-4}$ | 1.0 | 0.30 | 7.7 |
| $9.6 \cdot 10^{-4}$ | 2.0 | 0.50 | 7.20 |
| $14.4 \cdot 10^{-4}$ | 3.0 | 0.60 | 7.35 |
| $20.0 \cdot 10^{-4}$ | 4.2 | 0.70 | 7.2 |
| $3.1 \cdot 10^{-3}$ | 6.5 | 0.80 | 6.8 |
| $4.8 \cdot 10^{-3}$ | 10.0 | 0.85 | 7.85 |

mean 7.58

Table 3. Yield of niobium complexonate as a function of the EDTA concentration and calculation of the conditional instability constant of niobium complexonate. Nb_2O_5 concentration 1.5×10^{-4} M, pH 3.5 ($I = 0.4$; KCl).

| EDTA concn., c_Y | $A = \frac{c_Y}{c_{\text{Nb}}}$ | $B = \frac{I}{I_{\text{max}}}$ | $10^4 K$ |
|----------------------|---------------------------------|--------------------------------|----------|
| $0.75 \cdot 10^{-4}$ | 0.5 | 0.15 | 2.98 |
| $1.5 \cdot 10^{-4}$ | 1.0 | 0.30 | 2.44 |
| $3.0 \cdot 10^{-4}$ | 2.0 | 0.45 | 2.82 |
| $4.5 \cdot 10^{-4}$ | 3.0 | 1.23 | 2.98 |
| $6.0 \cdot 10^{-4}$ | 4.0 | 0.65 | 2.88 |
| $7.5 \cdot 10^{-4}$ | 5.0 | 0.68 | 3.04 |
| $9.0 \cdot 10^{-4}$ | 6.0 | 0.73 | 2.98 |
| $10.5 \cdot 10^{-4}$ | 7.0 | 0.75 | 3.13 |
| $1.5 \cdot 10^{-3}$ | 10.0 | 0.85 | 2.44 |
| $2.25 \cdot 10^{-3}$ | 15.0 | 0.94 | 1.34 |
| $3.0 \cdot 10^{-3}$ | 20.0 | 0.98 | 0.6 |

Mean 2.85

Indirect or Indicator Method

As was shown above, in the polarography of solutions of cadmium in hydrochloric acid (pH 2.7) containing EDTA, at a relative concentration of EDTA of $A = 1$ polarograms are observed which consist of two steps—the reduction of free cadmium ions and the reduction of the cadmium bound in the complexonate. The addition to such a solution of the polarographically inactive ions of a metal capable of reacting with EDTA (for example, Al or Mn) leads to a decrease in the yield of the cadmium complexonate. By

polarographically determining the value of the yield of cadmium complexonate $B = I/I_{\max}$ at a different concentration of aluminium or manganese, Eqn. (2) could be used to calculate the ratio of the conditional instability constants of aluminium and manganese to that of cadmium.

Table 4. Yields of cadmium complexonate in the presence of aluminium and calculation of the ratio of the conditional constants of cadmium and aluminium complexonates. $c_{\text{Cd}} = 8.9 \times 10^{-4}$, pH 2.7 ($I = 1.08$; $K_2\text{SO}_4$).

| Aluminium concn., c_{Al} | EDTA concn., c_{Y} | $A = \frac{c_{\text{Y}}}{c_{\text{Cd}}}$ | $\frac{c_{\text{Al}}}{c_{\text{Cd}}}$ | $B = \frac{I}{I_{\max}}$ | $\frac{K_{\text{Al}}}{K_{\text{Cd}}}$ |
|-----------------------------------|-----------------------------|--|---------------------------------------|--------------------------|---------------------------------------|
| — | $6.0 \cdot 10^{-4}$ | 0.675 | none | 0.64 | — |
| $8.9 \cdot 10^{-4}$ | $6.0 \cdot 10^{-4}$ | 0.675 | 1 | 0.50 | 4.7 |
| $17.10 \cdot 10^{-4}$ | $6.0 \cdot 10^{-4}$ | 0.675 | 2 | 0.45 | 6.0 |
| $27.7 \cdot 10^{-4}$ | $6.0 \cdot 10^{-4}$ | 0.675 | 3 | 0.35 | 3.7 |
| — | $4.45 \cdot 10^{-2}$ | 50 | | | |

Mean 3.7

Aluminium. Table 4 gives the results of the polarographic determination of the yield of cadmium complexonate in the presence of various concentrations of aluminium and the calculated ratio of the conditional instability constants of the aluminium and cadmium complexonates. Starting from the values obtained for the ratios of the constants, and bearing in mind that at pH 2.7 neither cadmium nor aluminium is hydrolysed, we calculated the concentration instability constant of the aluminium complexonate, $K_{\text{instab}} = 10^{-15.9}$, which agrees satisfactorily with the published value⁶ of $K = 10^{-16.13}$.

Table 5. Yield of bismuth complexonate in the presence of zirconium as a function of the EDTA concentration. Bismuth concentration 4.64×10^{-4} ($I = 3.6$; HNO_3).

| Zirconium concn., c_{Zr} | EDTA concn., c_{Y} | $A = \frac{c_{\text{Y}}}{c_{\text{Bi}}}$ | $B = \frac{I}{I_{\max}}$ | $\frac{K_{\text{Zr}}}{K_{\text{Bi}}}$ |
|-----------------------------------|-----------------------------|--|--------------------------|---------------------------------------|
| — | $2.4 \cdot 10^{-2}$ | 50 | — | — |
| $4.6 \cdot 10^{-4}$ | $4.64 \cdot 10^{-4}$ | 1.0 | 0.20 | 0.52 |
| $4.6 \cdot 10^{-4}$ | $9.27 \cdot 10^{-4}$ | 2.0 | 0.40 | 0.45 |
| $4.6 \cdot 10^{-4}$ | $12.70 \cdot 10^{-4}$ | 2.75 | 0.50 | 0.33 |
| $4.6 \cdot 10^{-4}$ | $15.3 \cdot 10^{-4}$ | 3.3 | 0.60 | 0.27 |
| $4.6 \cdot 10^{-4}$ | $23.20 \cdot 10^{-4}$ | 5.0 | 0.70 | 0.60 |
| $4.6 \cdot 10^{-4}$ | $36.0 \cdot 10^{-4}$ | 7.7 | 0.80 | 0.44 |

Mean 0.46

Manganese. We determined the concentration instability constant of manganese complexonate in a similar manner, $K_{\text{instab}} = 10^{-14.76}$, which also agrees satisfactorily with the published value⁶: $K_{\text{instab}} = 10^{-14.06}$.

Zirconium. There are few papers¹³⁻¹⁹ and these give contradictory values of estimates of the stability of zirconium complexonate. For example, $\text{p}K = 19.14$;¹³ $\text{p}K = 16.0$;¹⁴ $\text{p}K = 28-30$;¹⁵⁻¹⁶ $\text{p}K = 29$;^{17,18} and $\text{p}K = 28.9$.¹⁹ These variations must evidently be explicable in

terms of differences in the state of the zirconium in solutions of different acidity. Zirconium, which tends to hydrolyse and polymerise, exists as the free ion Zr^{4+} only at a solution acidity of ≤ 2 M. Clearly, the instability constant determined at pH 2 and 5^{13,14} relates to the zirconyl ion ZrO^{2+} .

The conditional instability constants of the zirconium complexonates were determined in nitric acid with bismuth as the indicator element. Table 5 gives the results of experiments on the effect of zirconium on the yield of bismuth complexonate.

Our results were used to construct a graph of the variation of the yield of bismuth complexonate with the relative concentration of EDTA in the presence of zirconium (Fig. 2b) and to calculate the ratio of the conditional instability constants of zirconium and bismuth complexonates, this was 0.46. Assuming that for bismuth $K_{\text{instab}} = 10^{-27.93}$, we obtain for zirconium $K_{\text{instab}} = 10^{-28.4}$, which agrees with most of the published values¹⁵⁻¹⁹.

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