

THE POTENTIOMETRIC TITRATION OF CALCIUM. II

BY

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The reversible electrode of the third order, lead amalgam — lead oxalate — calcium oxalate, is useful for the potentiometric titration of calcium ions with ammonium oxalate. The titration is however disturbed when magnesium and chlorine ions are present in too great a concentration.

The important role which the calcium ion fulfills in nature and particularly in biology gave rise to the question whether it is possible to determine calcium ion concentrations by electrical methods. The most attractive method, the potentiometric determination of calcium ion concentrations with an appropriate electrode, lead to the use of calcium fluoride plates as the electrode material¹⁾. The use of these electrodes meets in most cases with great difficulties which must be attributed to the material itself. The results of further investigations which are still partially incomplete, will be communicated later.

In an other method the calcium ion concentration is determined by potentiometric titration with ammonium oxalate. In a previous communication²⁾ were given the results of the potentiometric titration of calcium with ammonium oxalate, in which use was made of various electrodes of the third order. Among these electrodes are some which are useful when chlorine ions are also present in the solution.

Now that it appeared that Caris³⁾ had described a lead-lead oxalate-calcium oxalate electrode, it seemed profitable to include this electrode in the investigation. The results of this investigation are described in the present communication.

Le Blanc and Harnapp⁴⁾ had also already investigated this electrode but they got less favourable results in consequence of changes at the electrode which must probably be attributed to the formation

1) H. J. C. Tendeloo, J. Biol. Chem. 113, 333 (1936).

2) C. A. Nierstraz en H. J. C. Tendeloo, Rec. trav. chim. 53, 792 (1934).

3) Caris, Elektrochem. 44, 366 (1938).

4) Le Blanc und Harnapp, Z. physik Chem. (A). 166, 321 (1933).

of lead oxide and lead carbonate. We found that these disadvantages as well as others appear when lead amalgam of too high a concentration was used.

The electrode was made by dissolving chemically pure lead to a concentration of about 5 % in distilled mercury. This lead amalgam was placed in the wide portion of a glass apparatus as shown in fig. 1. The connection between the amalgam and the mercury column was obtained by the platinum wire which was sealed into the glass at A.

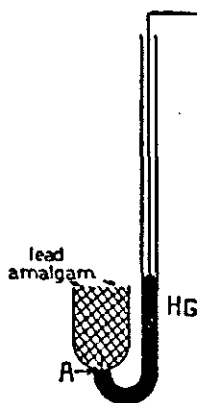


Fig. 1.

The solutions, which were titrated with ammonium oxalate, were saturated with lead oxalate. A saturated calomel electrode was used as the second half-cell, while the connection between the two half-cells was brought about in the customary way by means of an agar-KCl syphon and a saturated KCl-solution.

The e.m.f. of the cells, which were schematically composed as follows:

Lead amalgam	solution of a calcium salt saturated with lead and calcium oxalates	saturated KCl solution	saturated calomel electrode
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was measured with a Lautenschläger ionometer with vigorous stirring. The titrated solutions still had the same potential after standing for several days.

The reproducibility of the measurements appeared to be very good throughout, as is seen from table I, in which are given the figures for a titration of calcium oxalate carried out in sextuplicate.

Table I.

cm ³ ammonium oxalate added	Measured e.m.f. in millivolts					
10.0	592	592	592	592	593	592
11.0	—	594	593	593	594	593
12.0	599	599	599	597	599	599
13.0	612	612	611	609	610	612
14.0	623	624	624	—	620	—

(Titration of 10 cm³ calcium acetate, containing 25.2 mg calcium, diluted with 150 cm³ water with 0.0985 *n* ammonium oxalate solution. Found 25.6 mg).

Table II.

cm ³ calcium salt solution	10 cm ³ calcium-acetate			10 cm ³ calcium-chloride			20 cm ³ calcium-chloride		
mg calcium	23.7			16.7			33.4		
cm ³ water added	150 cm ³			150 cm ³			140 cm ³		
Normality NH ₄ -oxalate	0.1000			0.1000			0.1000		
	V	E	$\frac{\Delta E}{\Delta V}$	V	E	$\frac{\Delta E}{\Delta V}$	V	E	$\frac{\Delta E}{\Delta V}$
	10.0	575.0		6.0	580.0		16.0	573.0	
	11.0	576.0	1.0	7.0	581.0		16.2	574.0	1.0
	11.2	579.0	2.2	8.0	586.7	3.0	16.4	576.0	2.0
	11.4	581.2	2.6	8.2	589.7	3.3	16.6	579.3	3.3
	11.6	583.8	3.2	8.4	593.0	4.3	16.8	582.5	3.2
	11.8	587.0	4.7	8.6	597.3	3.7	17.0	585.8	3.3
	12.0	591.7	4.0	8.8	601.0	3.2	17.2	590.0	4.2
	12.2	595.7	3.5	9.0	604.2		17.4	593.8	3.8
	12.4	599.2	2.3				17.6	597.5	3.7
	12.6	601.5	2.5				17.8	600.0	2.5
	12.8	604.0					18.0	602.3	2.3
mg calcium found	23.9			17.0			34.2		

The calcium concentration of the solutions was determined gravimetrically.

Table III.

cm ³ solution	10 cm ³ calcium-chloride 10 cm ³ sodium-chloride	10 cm ³ calcium-chloride 10 cm ³ potassium-chloride
mg calcium	16.7 mg	16.7
mg sodium	19.2 mg	—
mg potassium	—	32.6
cm ³ water added	140 cm ³	140 cm ³
Normality of NH ₄ -oxalate	0.1000	0.1000
	V E $\frac{\Delta E}{\Delta V}$	V E $\frac{\Delta E}{\Delta V}$
	7.0 581.0	7.0 581.0
	8.0 586.5 2.5	8.0 585.5 2.5
	8.2 589.0 2.5	8.2 588.0 3.0
	8.4 591.5 3.5	8.4 591.0 4.0
	8.6 595.0 2.5	8.6 595.0 2.7
	8.8 597.5 2.0	8.8 597.7 2.0
	9.0 599.5 1.8	9.0 599.7 2.3
	9.2 601.3 1.7	9.2 602.0 3.0
	9.4 603.0	9.4 605.0
mg calcium-found	17.0	17.0

The results of a few titrations are collected in table II. The end-point of the titration was calculated by Hahn and Frommer's method⁵⁾.

In the titration of calcium chloride it was found that a chlorine ion concentration of about 0.03 *n* impeded the establishment of a constant e.m.f. If however the solution was diluted ten times this difficulty did not occur. The electrode, as was to be expected, is not entirely insensitive to chlorine ions.

⁵⁾ See Erich Müller, *Elektrometrische Massanalyse*, 5th ed. p. 79.

It was our intention to investigate whether the potentiometric titration of calcium we have worked out could be applied to milk. The titration of skim milk and dissolved skim milk powder did not however succeed because it was impossible to obtain a constant setting of the potential. Apart from other causes there is the possibility that other ions influence the titration of calcium unfavourably. Thus *C a r i s* states that sodium ions disturb the titration. As can be seen from table III, it appeared from our research that there is no disturbance by an equivalent amount of sodium ions nor by an amount of potassium equivalent to the calcium. The electrode must be cleaned before each measurement since otherwise the final value of the potential is reached very slowly.

Table IV.

cm ³ solution	10 cm ³ calcium-chloride 10 cm ³ magnesium-chloride	10 cm ³ calcium-chloride 30 cm ³ magnesium-chloride
mg calcium	16.7 mg	36.4
mg magnesium	1.5 mg	4.5
cm ³ water added	140 cm ³	120
Normality NH ₄ -oxalate	0.1000	0.0985
	V E $\frac{\Delta E}{\Delta V}$	V E $\frac{\Delta E}{\Delta V}$
	7.0 583.0	10.0 600.5
	8.0 589.0	15.0 604.5
	8.4 594.0	16.0 605.0
	8.8 599.5	17.0 609.5
	9.2 603.0	18.0 615.5
	9.6 606.5	19.0 624.5
	10.0 609.0	20.0 631.0
		21.0 636.0
calcium found	17.0	36.5

The presence of magnesium was however found to disturb the titration. The ratio Ca : Mg in milk is about 9 : 1. The titration of

36.4 mg of calcium in the presence of 4.5 mg of magnesium is successful, as also that of 16.7 mg of calcium in the presence of 1.5 mg of magnesium. If however there are 3.0 mg of magnesium present with 16.7 mg of calcium, it no longer succeeds.

The influence of magnesium on the gravimetric determination of calcium has been investigated thoroughly by Richards⁶⁾.

The results are given in table IV.

In pure solutions of calcium chloride a constant potential is not established. Three solutions of calcium chloride were made containing 365.0, 36.5 and 3.65 mg of calcium per litre respectively. Each of the solutions was saturated with lead and calcium oxalates. Table V gives the results of the measurements.

Table V.

mg calcium per litre	e. m. f. measured without stirring in millivolts.	e. m. f. measured two days later with stirring in millivolts.
365.0	586	575
36.5	616	605
3.65	640	632

The difference in potential of 29 millivolts to be expected theoretically for a tenfold dilution of the solutions was found very approximately. The measured e. m. f. was however found to depend on whether the solution is stirred or not.

Without stirring the e. m. f. was found to rise 10 millivolts; if however the solution was stirred for a long time before the measurement, the e. m. f. fell more than it had first risen. Addition of about 0.1 milliequivalent of ammonium oxalate however abolishes these changes due to stirring, so that the potential, as was the case in the titrations, remained constant.

Although certain objections are still connected with the potentiometric determination of calcium ion concentrations with the electrode described here, the results given in table V justify the expectation that further research will lead to improvements, whereby potentiometric determinations of calcium at a concentration of about 0.2 milliequivalent per litre would become possible.

Wageningen, *Laboratory for Physical and Colloid Chemistry*,
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⁶⁾ Richards, Z. anorg. Chem. 28, 71 (1901).