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THE COMPLEXOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM. A CRITICAL STUDY

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Summary—A critical examination has been made at the 0·01*M* level of the performance of various indicators for the titration of calcium in the presence or absence of magnesium with EDTA. The *bis*-azo dye Acid Alizarin Black SN is recommended for the titration of calcium in pure solution, and for solutions where the magnesium/calcium ratio does not exceed 1:12. For higher ratios, quantitative recovery of calcium and satisfactory end-points are only obtained when Calcon is used as indicator.

The range of application of Acid Alizarin Black SN can be extended if 1:2-diamino-propane N:N'-tetra-acetic acid is used in place of EDTA as titrant.

IN THE original procedure of Schwarzenbach, Biedermann and Bangerter[1] total hardness is determined in the presence of Solochrome Black T as indicator at pH 10; calcium is determined at pH > 12, in the presence of the precipitated magnesium

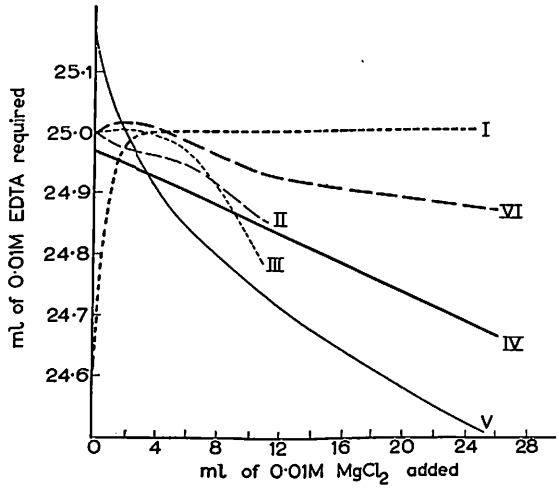

FIG. 1. Recovery of 25·00 ml of 0·01*M* calcium in the presence of magnesium.
I Calcon; II Methyl Thymol Blue; III Acid Alizarin Black SN; IV Murexide; V Calcein; VI Acid Alizarin Black SN with 1:2-Diaminopropane-N:N'-tetra-acetic acid.

hydroxide, with Murexide as indicator. Several other indicators have since been advocated. The present paper describes an examination we have made of several of these indicators. Where possible the indicators have been used under standardised conditions except for some variation in the reagents used for adjustment of the necessary pH conditions.

Fig. 1 shows the recovery of calcium obtained in the presence of varying amounts of magnesium when using the different indicators. These titrations were carried out

at the 0·01*M* level. The various indicators are also considered separately; details of indicator response and tables of results are given showing the variation in recovery of calcium.

Each entry in the tables represents the mean of ten titrations. A measure of the reproducibility of each indicator may be deduced from the standard deviation. More than 350 determinations were carried out.

Murexide

When no magnesium is present, the pink to purple end-point in the EDTA titration of calcium is sharp but the colour contrast is poor, though it may be improved by screening.[2] Our results show a tendency for low recoveries to occur even in the absence of magnesium, but this may be partly due to personal reactions to the colour change of the indicator.

TABLE I.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, MUREXIDE AS INDICATOR

ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	24·97	0·03
25·00	1·00	24·96	0·03
25·00	2·00	24·95	0·02
25·00	5·00	24·91	0·05
25·00	10·00	24·84	0·05
25·00	25·00	24·68	0·07

The error in the recovery of calcium appears to be proportional to the amount of added magnesium, and the quality of the end-point deteriorates progressively both with regard to sharpness and colour contrast. In these titrations, diethylamine was used as the buffer substance. In our experience this affords a better colour change than the conventional sodium or potassium hydroxide reagents.

Calcein

Calcein[3] screened with thymolphthalein[4] gives a sharp end-point from fluorescent green to dark red in the titration of calcium in pure solution. The recovery of calcium appears to be high when the indicator is titrated to a definite colour change, but this may be due to the presence of impurities in the commercial sample of indicator which we used. When magnesium is present, the end-point is less sharp and the green fluorescence does not entirely disappear, though the dark red colour is very strong in transmitted light. The recovery of calcium falls off markedly as the ratio of magnesium to calcium is increased. The indicator action is also complicated by the occurrence of premature end-points before the equivalence-point. Furthermore, the green fluorescence reappears less than a minute after the end-point.

With this indicator, either sodium or potassium hydroxide was preferred to diethylamine for the adjustment of pH since the last mentioned base tended to cause premature end-points and colour reversion.

TABLE II.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, CALCEIN AS INDICATOR
ml of 0·01M solutions

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·16	0·07
25·00	1·00	25·06	0·03
25·00	2·00	24·99	0·04
25·00	5·00	24·87	0·03
25·00	10·00	24·75	0·05
25·00	25·00	24·51	0·04

Methyl thymol blue

This substance, which was recently proposed by Körbl and Přibil,[5] gives a sharp, easily detected blue to colourless end-point in the titration of calcium in pure solution. The recovery of calcium appears to be quantitative. When the magnesium/calcium ratio is greater than 1:5, premature end-points occur, but the colour reverts to blue in *ca.* 10 seconds. This reversion also occurs beyond the equivalence-point.

TABLE III.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, METHYL THYMOL BLUE AS INDICATOR
ml of 0·01M solutions

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·03
25·00	1·00	24·98	0·02
25·00	2·00	24·97	0·02
25·00	5·00	24·96	0·01
25·00	10·00	24·87	0·02
25·00	25·00	—	—

The end-point was judged to be that point in the titration at which the colour reversion no longer occurs quickly—as it does with the first premature end-points. When the magnesium/calcium ratio approached unity, it was not found possible to obtain reproducible results because of the profusion of premature end-points and the repeated reversion of colour even beyond the equivalence-point.

Diethylamine was used as the buffer substance, but caustic soda serves equally well provided that care is taken not to raise the pH much above 12·5. The indicator is permanently blue at higher pH values.

Calcon (B.C.I. No. 202)

Calcon, proposed by Hildebrand and Reilley,[6] does not give a sharp end-point when calcium is titrated with EDTA in the absence of magnesium, or when the magnesium/calcium ratio is less than 1:12. The recovery of calcium is markedly low,

cf. Table IV. The indicator shows a long purple intermediate shade with a diminishing red shade which finally disappears leaving a pure blue solution *before* the equivalence point, *cf.* Fig. 1. The colour change may spread over 6–8 drops of 0·01*M* titrant. However, the quality of the end-point improves markedly with increasing amounts of magnesium, so that for magnesium/calcium ratios between 1:10–1:5 sharp end-points are obtained and the recovery of calcium appears to be quantitative.

TABLE IV.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, CALCON AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	24·63	0·10
25·00	1·00	24·86	0·10
25·00	2·00	24·99	0·03
25·00	5·00	25·00	0·06
25·00	10·00	24·99	0·07
25·00	25·00	25·01	0·06

In the presence of larger amounts of magnesium, brief premature end-points appear before the equivalence point, but since these revert in 2–3 seconds it is possible to locate the true end-point without much difficulty. Even beyond the equivalence-point, reversion of colour from blue to purple-red occurs after a period of more than 10 seconds. Diethylamine was used as the buffer substance.

Hildebrand and Reilley applied Calcon to the titration of solutions having much higher ratios of magnesium to calcium (10 molar proportions). They comment that the end-point is sluggish when there is a heavy precipitate of magnesium hydroxide.

Acid Alizarin Black SN (B.C.I. No. 337)

In a previous publication, we proposed the use of this *bis*-azo dye for the titration of calcium.[7] In the absence of magnesium, or with magnesium/calcium ratios less

TABLE V.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, ACID ALIZARIN BLACK SN AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·01
25·00	0·50	24·99	0·03
25·00	1·00	25·00	0·01
25·00	2·00	24·99	0·02
25·00	5·00	24·97	0·05
25·00	10·00	24·81	0·12
25·00	25·00	—	—

than 1:12, a very sharp red to turquoise-blue end-point is obtained and the recovery of calcium appears to be quantitative.

In the presence of larger amounts of magnesium, the end-point response of the indicator becomes less well defined; the colour changes through purple and blue to turquoise-blue. In addition, the recovery of calcium falls below the theoretical value. In the presence of large amounts of magnesium the titration should be carried through to the final shade, but the intermediate colours may spread over 8–10 drops. Brief reversion of colour occurs before the equivalence-point as with the other indicators, but beyond equivalence the end-point is stable for several minutes.

Diethylamine was used as the buffer substance.

Titration of calcium in the presence of magnesium with 1:2-*diaminopropane*-N:N′-*tetra-acetic acid*

As a result of work being carried out in this laboratory on various chelating agents related to EDTA,[8] we have examined the application of 1:2-diaminopropane-N:N′-tetra-acetic acid to this titration. Our examination was confined to the use of Calcon and Acid Alizarin Black SN as indicators, since these appeared to be the most suitable substances in the light of our previous experiments using EDTA. It was found that no better result was obtained when using Calcon—indeed we prefer the use of EDTA in conjunction with the indicator, but the performance of Acid Alizarin Black SN was considerably improved.

TABLE VI.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM WITH 1:2-DIAMINOPROPANETETRA-ACETIC ACID, ACID ALIZARIN BLACK SN AS INDICATOR

ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·00
25·00	1·00	25·00	0·03
25·00	2·00	25·02	0·04
25·00	5·00	25·01	0·05
25·00	10·00	24·93	0·06
25·00	25·00	24·88	0·08

Very sharp end-points and quantitative recoveries of calcium were obtained when the magnesium/calcium ratio did not exceed one fifth. Thereafter, increasingly large amounts of magnesium caused less sharp end-points and low recoveries of calcium. It would appear from Fig. 1 that slightly high results are obtained for low magnesium contents, but it must be stressed that the results shown are the arithmetic mean titres and the divergence from theory is within the limits of measurement of the 50-ml burettes used in these experiments.

EXPERIMENTAL

Reagents

0·01*M EDTA:* Standardised against pure magnesium metal using Solochrome Black 6B at pH 10 as indicator.[9]

0·01*M Calcium chloride:* Prepared from A.R. calcium carbonate by dissolution in a slight excess of hydrochloric acid.

0·01*M Magnesium Chloride:* Prepared from pure magnesium metal.

Buffers: Diethylamine
2*N* Sodium or potassium hydroxide

Indicators: Calcon—0·5% Ethanolic solution
Murexide—1% Dispersion in sodium chloride.
Calcein—1% Calcein, 0·6% thymolphthalein dispersion in potassium chloride
Methyl Thymol Blue—1% Dispersion in potassium nitrate
Acid Alizarin Black SN—2% Dispersion in sodium chloride.

Procedure

25·00 ml of 0·01*M* calcium chloride solution were pipetted into a 250-ml conical flask and the requisite amount of magnesium chloride solution was added from a burette. To every 25 ml of this test solution were added 5 ml of diethylamine or 5 ml of alkali hydroxide. The mixture was shaken and allowed to stand for 5 minutes. A sufficient amount of the appropriate indicator was then added to impart the necessary colour to the solution and the titration was carried out with 0·01*M* EDTA to the end-point. Ten determinations were made for each molar ratio of calcium to magnesium and the mean recovery and standard deviation were recorded in each case.

DISCUSSION

As a result of these studies it appears to us that the conventional Murexide indicator for the titration of calcium in the presence of magnesium is less suitable than some of the newer indicators both on the grounds of low recoveries of calcium and the quality of the end-point. The presence of appreciable amounts of magnesium causes a deterioration in the quality of the end-point of all these indicators except Calcon and favours low recoveries. The behaviour of Calcon is unsatisfactory in the absence of magnesium hydroxide, but is considerably improved in its presence. For calcium in the absence of magnesium all the other indicators examined, except possibly Calcein and Murexide, are satisfactory, but the most precise and clear-cut end-point is obtained with Acid Alizarin Black SN. This indicator is particularly useful in that it functions best in the region of magnesium/calcium ratios where Calcon cannot be applied very successfully, *cf.* Fig. 1. Accordingly we recommend that Acid Alizarin Black SN be used for the titration of calcium in pure solution and for magnesium/calcium ratios less than 1:12 (0·01*M* solutions); for higher ratios of magnesium to calcium, Calcon should be applied.

The occurrence of premature end-points is almost certainly due to the co-precipitation of calcium with the magnesium hydroxide, but the reversion of colour which occurs even after the equivalence-point with those indicators which are capable of responding to magnesium ions with a high degree of sensitivity, *viz* Methyl Thymol Blue, Calcein and Calcon, suggests that the magnesium takes part in the reaction either by direct solution of the hydroxide precipitate or by kinetic exchange with the chelated calcium in the solution.

The indicator of Patton and Reeder[10] was not included in this comparison, because in spite of its excellent colour change in the titration of calcium in the presence of magnesium, in our experience it is somewhat unstable in strongly alkaline solution.

The extension of the range over which Acid Alizarin Black SN gives a sharp end-point with quantitative recoveries of calcium when 1:2-diaminopropane-N:N′-tetra-acetic acid is used as titrant is interesting, but in view of the excellent response of Calcon with EDTA in this extended region, there is little advantage to be gained.

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Zusammenfassung—Es wurde eine kritische Untersuchung verschiedener Indikatoren für die Titration von Calzium mit 0·01*M* Lösung von ÄDTA in Anwesenheit oder Abwesenheit von Magnesium gemacht. Der *bis*-azo Farbstoff Acid Alizarin Black SN wird für die Titration von Calzium in reiner Lösung vorgeschlagen sowie für Lösungen in denen das Magnesium/Calzium Verhältnis 1:12 nicht übersteigt. Bei Größeren Verhältnissen wird nur dann Calzium quantitativ erfasst und eine gute Endpunkt erhalten, wenn Calcon als Indikator gebraucht wird.

Man kann den Anwendungsbereich von Acid Alizarin Black SN ausdehnen, wenn 1:2-Diaminopropan-N:N'-Tetraessigsäure and Stelle von ÄDTA als Masslösung gebraucht wird.

Résumé—Un examen critique a été fait à partir des solutions 0·01*M* du fonctionnement de divers indicateurs utilisés pour le titrage du calcium, soit suel, soit en présence de magnésium, au moyen de l'EDTA. Le colorant *bis*azoïque "Acid Alizarin Black SN" est recommendé pour le titrage du calcium en solution pure, et pour des solutions où le rapport magnésium/calcium ne dépasse pas 1:12. Où les rapports sont plus hauts la récupération quantitative du calcium et des fins de réaction satisfaisantes ne sont obtenues qu'en utilisant comme indicateur le calcon.

On peut porter plus loin les limites d'application de l'Acid Alizarin Black SN en remplaçant l'EDTA comme solution titrante par l'acide 1:2-diamine-propane-N:N'-tetracétique.

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