The Selective Titrations of Calcium in the Presence of Magnesium

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The chelometric determination of calcium in the presence of magnesium is carried out by using ethylenediaminetetraacetic acid (EDTA) as a titrant at pH 12~13. Magnesium is precipitated as the hydroxide, and murexide, thymolphthalein complexone (TPC), Calcon or Patton-Reeder's reagent[1] (NN) is used as an indicator. However, the presence of precipitated magnesium hydroxide causes a coprecipitation of calcium and an adsorption of the metal indicator on the precipitate, and these behaviors interfere to find an end-point of reaction accurately. Some attempts to overcome them have been reported. For example, to prevent the precipitation, tartrate[2] or sucrose[3,4] was added. Although the precipitate was thereby avoided, the end-point was indefinite. This is because of the small difference in the stability constants of calcium- and magnesium-EDTA complexes ($\log K_{CaZ}=10.70$, $\log K_{MgZ}=8.69$).

Instead of using EDTA as a titrant for calcium in the presence of magnesium, glycoletherdiaminetetraacetic acid (GEDTA) could be introduced; the difference between the stability constants of calcium- and magnesium-GEDTA complexes is 5.8 in $\log K$ units ($\log K_{CaZ}=11.0$, $\log K_{MgZ}=5.2$), and therefore the selective titration of calcium in the presence of magnesium would be possible at pH 10 where magnesium remains in the solution. However, a selective indicator for calcium at pH 10 has not yet been found. A potentiometric end-point detection by the mercury electrode[5], and an indirect end-point indication using the zinc-zincon system[6] have been proposed. Unfortunately both methods somewhat restrict the use of certain important masking agents which are often employed in practical analyses.

Burg and Conaghan[7] achieved the selective titration of calcium in the presence of magnesium with GEDTA, using tartrate as a masking agent for magnesium and Calcon as an indicator at pH 13 and at about 40°C.

In this paper, the work of masking agents and indicators on the chelometric determination of calcium in the presence of magnesium is reported. Some applications for limestone, dromite and magnesite will be presented.

Experimental and Results

Reagents.—A 0.01 M EDTA solution was prepared by dissolving 3.73 g. of EDTA (disodium salt) in 1 l. of distilled water. A 0.01 M GEDTA solution was prepared by dissolving 3.8 g. of glycoletherdiaminetetraacetic acid in 20 ml. of 1 N sodium hydroxide and then by diluting this solution with redistilled water to 1 l. A 0.01 M calcium solution; dissolve 1.0009 g. of calcium carbonate in hydrochloric acid, add distilled water, and heat to remove the carbon dioxide. After cooling, dilute with distilled water to 1 l. The 0.01 M EDTA and GEDTA solutions were standardized with this solution. The 0.1 M magnesium solution was prepared by dissolving 24.65 g. of magnesium sulfate heptahydrate in a small volume of distilled water and by diluting this solution. to 1 l.

The BT solution was prepared by dissolving 0.5 g. of Eriochrome Black T and 4.5 g. of hydroxylamine hydrochloride in 100 ml. of methanol. The Dotite NN solution was prepared by dissolving 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (Patton-Reeder's reagent) in methanol. For the buffer solution, 7 g. of ammonium chloride and 57 ml. of concentrated aqueous ammonia were dissolved in 100 ml. of distilled water. The tartrate solution was prepared by dissolving 10 g. of potassium sodium tartrate in 100 ml. of distilled water.

Indicators.—The optimum pH ranges for several indicators were studied. Various pH solutions were prepared using aqueous ammonia or potassium and sodium hydroxide. A small amount of an indicator was added to each of them, and the stability of the color was examined. Further, the color of the free indicator was compared with that of the calcium complex. The indicators, their optimum pH ranges, and the methods of preparation are shown in Table I.

It was tested whether or not, in the calcium titration, these indicators indicated the accurate quantitative value, with sharp color changes. These tests were carried out in the following

1) J. Patton and W. Reeder, *Anal. Chem.*, **28**, 1026 (1956).
2) V. Tikkomirova and O. Simackova, *Collection*, **22**, 982 (1957).
3) R. D. Bond and B. M. Tuker, *Chem. & Ind.*, **1954**, 1236.
4) B. M. Tuker, *Analyst*, **82**, 284 (1957).
5) R. W. Schmid and C. N. Reilly, *Anal. Chem.*, **29**, 264 (1957).
6) F. S. Sadek, R. W. Schmid and C. N. Reilly, *Talanta*, **2**, 38 (1959).
7) R. A. Burg and H. F. Conaghan, *Chemist-Analyst*, **49**, 100 (1960).

TABLE I

Indicator	Optimum pH range	Preparation
Calcein (Fluorescein complexone)	12.9～13.1	Diluted 1 : 100 with KNO_3
MTB (Methylthymolblue)	11.9～12.5	Diluted 1 : 100 with KNO_3
TPC (Thymolphthalein complexone)	10.4～12.0	Diluted 1 : 100 with K_2SO_4
PC (*o*-Cresolphthalein complexone)	10.5～11.0	0.1% PC in methanol
Calcon (1-(2-Hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid)	11.8～12.2	0.5% Calcon in methanol
NN	13.3～13.5	Dotite NN solution

way: Take 10 ml. of a 0.01 M calcium solution and dilute to about 50 ml. with distilled water. Adjust pH and add a small amount of an indicator. Titrate with 0.01 M GEDTA.

The results of these analyses are given in Table II.

TABLE II

Indicator	ca. 0.01 M GEDTA required (ml.)	Nature of end-point
Calcein	10.66±0.01	Sharp
MTB	10.67±0.01	Very sharp
TPC	10.64±0.01	Sharp
PC	10.65±0.06	Fairly sharp*
Calcon	—	Indefinite**
NN	10.67±0.01	Sharp

* Influenced by the amount of the indicator.
** Needs the presence of magnesium.

In the presence of tartrate to prevent the precipitation of magnesium hydroxide, it was investigated whether or not these indicators changed their colors at the end-point and also whether the color changes indicated the accurate quantitative value by this method: Take 10 ml. of a 0.01 M calcium solution and dilute to about 50 ml. with distilled water. Add 2 ml. of a 0.1 M magnesium solution and 2 ml. of a tartrate solution. Adjust pH and add a small amount of an indicator. Titrate with 0.01 M GEDTA.

For Calcein, MTB, TPC and PC, these color changes at the end-point were indefinite. These indicators could, therefore, not be used for this titration.

Calcon was tested according to the procedure proposed by Burg and Conaghan. It changed the color sharply at the end-point. However, because of warming the sample up to about 40°C before the titration, magnesium tended to precipitate. NN was also used in this titration at room temperature, but it took some time for the color to change completely. Both Calcon and NN indicated the correct end-point by MTB in the absence of magnesium.

Masking Agents.—Because many magnesium complexes are the O, O co-ordinated chelates, the suitable masking agents for magnesium at pH 12～13 would be expected to be found among organic substances having oxygen atoms capable of co-ordinating with magnesium. Several masking agents for magnesium were tested; the results were shown in Table III. The test solution was prepared by diluting 10 ml. of 0.01 M calcium and 5 ml. of a 0.01 M magnesium solution to 50 ml. with distilled water and by adding one of the masking agents. The pH value of the solution was adjusted to 13 and 13.5 by potassium and sodium hydroxide. Then we investigated to see whether or not the precipitate was formed at pH 13 and 13.5.

Among the masking agents shown in Table III, tartrate and gluconic acid were found to be the most suitable masking agents for magnesium at pH 13.5.

TABLE III. MASKING AGENTS FOR MAGNESIUM

Masking agent		Precipitation*	
Name	Amount	pH 13	pH 13.5
Glycolic acid (70%)	0.5 ml.	×	×
Lactic acid (75%)	0.5 ml.	○	×
Maleic acid	0.1～0.5 g.	×	×
Potassium sodium tartrate 4 aq. (10%)	2 ml.	○	○
Sodium citrate 2 aq. (10%)	2 ml.	○	×
Aconitic acid	0.1～0.5 g.	×	×
Glucronic acid	0.1 g.	×	×
Glucose (20%)	1 ml.	×	×
Potassium *d*-saccharate	0.1～0.5 g.	×	×
Potassium manno-saccharate	0.1～0.5 g.	×	×
Gluconic acid (50%)	1 ml.	○	○
Mucic acid	0.1 g.	×	×
Sucrose (20%)	1 ml.	×	×
Sodium alginate	0.1～0.5 g.	×	×
Sulfosalicylic acid	0.2 g.	×	×

*×: As soon as the alkaline solution was added, the precipitation occured.
○: The precipitate had not formed after more than about 10 min.

To compare tartrate with gluconic acid, the following experiment was carried out.

A test solution was prepared by diluting 10 ml. of 0.01 M calcium and 2 ml. of 0.1 M magnesium to 50 ml. with distilled water. Then

TABLE IV. TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM WITH GEDTA USING NN INDICATOR

0.01 M Ca taken ml.	0.1 M Mg taken ml.	0.35 M Tartrate taken ml.	ca. 0.01 M GEDTA required ml.	Nature of end-point
10.00	0.0	0.0	10.67±0.01	Very sharp (MTB as an indicator)
10.00	0.0	1.0	—	Indefinite
10.00	0.5	1.0	10.75±0.07	Indefinite (pptd)
10.00	1.0	1.0	10.68±0.01	Sharp
10.00	2.0	1.0	10.69±0.02	Fairly sharp
10.00	0.0	2.0	—	Indefinite
10.00	0.5	2.0	10.72±0.03	Fairly sharp (pptd)
10.00	1.0	2.0	10.67±0.02	Fairly sharp
10.00	2.0	2.0	10.66±0.01	Sharp
10.00	3.0	2.0	10.66±0.01	Sharp
10.00	4.0	2.0	10.67±0.02	Fairly sharp
10.00	5.0	2.0	10.67±0.10	Indefinite (pptd)
10.00	3.0	3.0	10.66±0.05	Sharp
10.00	4.0	3.0	—	Indefinite (pptd)
10.00	4.0	4.0	10.69±0.01	Sharp
10.00	5.0	4.0	10.84±0.15	Indefinite (pptd)
10.00	5.0	5.0	10.67±0.03	Sharp
10.00	6.0	5.0	10.67±0.02	Sharp
10.00	7.0	5.0	10.66±0.03	Fairly sharp
10.00	8.0	5.0	10.71±0.40	Indefinite (pptd)
10.00	8.0	6.0	10.94±0.40	Indefinite (pptd)
10.00	10.0	10.0	—	Indefinite (pptd)
10.00	10.0	12.0	—	Indefinite (pptd)
2.00	7.0	5.0	2.14±0.02	Sharp

2 ml. of a tartrate solution or 2.5 ml. of 5% gluconic acid, 2 ml. of 8 N potassium hydroxide, and a few drops of NN solution were added, and the solution was titrated with 0.01 M GEDTA.

In the presence of gluconic acid, the color change from red to blue at the end-point was proceeding slowly, and the amount of 0.01 M GEDTA was 0.2 ml. smaller than that of the correct end-point as indicated by MTB in the absence of magnesium. On using tartrate, there was a clearer difference than with gluconic acid between the color just before and after the end-point, and the amount of 0.01 M GEDTA consumed was the same as the correct equivalent value.

Magnesium Amount and Tartrate Amount. — With an increase in the concentration of magnesium, the concentration of tartrate should also be increased. The relation between the amounts of magnesium and of tartrate is shown in Fig. 1 and Table IV.

It was found that the maximum concentrations of magnesium and tartrate were 7 ml. of a 0.1 M magnesium solution (about 7×10^{-4} mol.) and 5 ml. of a tartrate solution (about 1.7×10^{-3} mol.).

The color at the end-point upon using the NN solution is light blue and somewhat differs from that of the calcium titration in the absence of tartrate and magnesium.

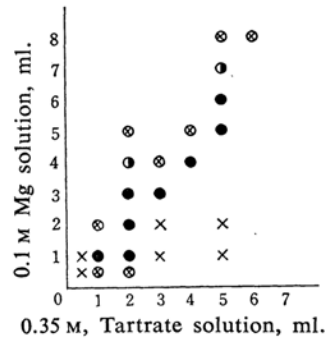

Fig. 1. The relation of magnesium and tartrate amounts.
× : Precipitated.
⊗ : Precipitated during the titration and the end-point was indefinite.
● : Given the accurate end-point indicated by MTB in the absence of magnesium.
◑ : Given the approximately accurate end-point.

Procedure for Limestone, Dromite and Magnesite.—Pulverize and dry samples for 2 hr. at 110°C and cool in a desiccator. Weigh out 1.0000 g. of each sample and dissolve it in a

TABLE V. DETERMINATION OF CALCIUM AND MAGNESIUM IN LIMESTONE, DROMITE AND MAGNESITE

Sample	Test solution (5 ml.)		Sample (1.0000 g.)	
	0.01 M EDTA* required ml.	0.01 M GEDTA** required ml.	CaO g.	MgO g.
Limestone (Sampo Kozan, Kawakami-gun, Okayama)	19.96±0.01	21.09±0.02	0.5538	0.0044
Limestone (Bisei-cho, Okayama)	19.83±0.01	21.01±0.03	0.5516	0.0034
Dromite (Ikura, Niimi-shi, Okayama)	19.62±0.01	14.83±0.02	0.3894	0.1154
Dromite (Ikura, Niimi-shi, Okayama)	19.21±0.01	18.17±0.02	0.4771	0.0444
Magnesite (Karube, Atetsu-gun, Okayama)	21.90±0.02	0.70±0.05***	0.0092	0.4352

* Factor=1.0007
** Factor=0.9363
*** Test solution: 10 ml.

small amount of dilute hydrochloric acid by heating. If the solution is turbid, leave it to stand for about 12 hours, filter and wash the precipitate with water. Dilute the filtrate in a 250 ml. measuring flask with distilled water. The solution is used as a test solution.

Determination of the Total Amount of Calcium and Magnesium.—Take 5 ml. of the test solution and dilute to about 50 ml. with distilled water. Add 1 ml. of 0.1 M Mg-EDTA, 1 ml. of a buffer solution, 3 drops of a 10% potassium cyanide solution (and triethanolamine, if necessary), and a few drops of a BT solution. Titrate with 0.01 M EDTA.

Determination of Calcium.—For limestone and dromite, take 5 ml. of the test solution and dilute to about 50 ml. with distilled water. Add 2 ml. of a 0.1 M Mg solution, 2 ml. of a tartrate solution, 2 ml. of 8 N potassium hydroxide, 3 drops of 10% potassium cyanide (and triethanolamine, if necessary), and a few drops of an NN solution, and titrate with 0.01 M GEDTA. For magnesite, take 10 ml. of the test solution and dilute to about 50 ml. with distilled water. Add 5 ml. of a tartrate solution and titrate with the procedure mentioned above, or titrate it after adding a known amount of calcium to the aliquot. Calculate by deducting the known amount of calcium. In this paper, the amount of calcium in magnesite was analysed by both two procedures and the two values were averaged.

Determination of Magnesium.—Magnesium is calculated by deducing the calcium from the calcium and the magnesium. The results of the analyses of limestone, dromite and magnesite are given in Table V.

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