Separation of Magnesium and Calcium by Ion Exchange Method

Application to Silicate and Carbonate Rocks

By

Takeshi SOTOBAYASHI

(Department of Chemistry)

(Received, December 3, 1961)

The determination of magnesium and calcium by titration with standard solution of disodium dihydrogen (ethylenedinitrilo-) tetraacetate (Versenate) has been investigated thoroughly and widely accepted. Following the original work of Biedermann and Schwarzenbach, several workers utilized the titration for determination of magnesium and calcium. The calcium was precipitated as the oxalate*[1,2] or sulfite*[3] and after filtration the magnesium was titrated using Eriochrome Black T as the indicator. Furthermore, Schwarzenbach *et al.* and others*[4,5] showed that calcium could be titrated with standard Versenate solution in the presence of magnesium at pH 12-13, ammonium purpurate being used as the indicator. More recently Diehl and Ellingboe*[6], and Patton and Reeder*[7] have reported more excellent indicators for calcium, calcein and 2-hydroxyl-1-(2-hydroxy-4-sulfo-1-naphthylazo) 3 naphtoic acid, respectively. On the other hand, Campbell and Kenner*[8] proposed a method which involved the separation of magnesium alone by employing a cation resin column instead of the removal of calcium by precipitation. As a rule, these methods involve two titrations, a titration for total magnesium and calcium, using Eriochrome Black T as the indicator and a titration of either of them. For the determination of the magnesium and calcium by the existed procedures some difficulties were experienced in regards to the titration error and the completeness of separation, especially a precipitating reagent being used. Thus in the present work the major objective is to develop the complete separation of magnesium and calcium by cation exchange chromatography followed by the separate determination of

---

*[1]. Diehl, H., Goetz, C. A., Hach, C. C., J. Am. Water Works Assoc. 42, 40 (1946).

*[2]. Banewicz, J. J., Kenner C. T., Anal. Chem. 24, 1186 (1952).

*[3]. Gehrke, C. W., Affsprung, H., Lee, Y., Anal. Chem. 26, 1944 (1954).

*[4]. Schwarzenbach, G., Biedermann, W., Bangerter, F., Helv. Chim. Acta, 29, 811 (1946).

*[5]. Cheng, K. L., Kurtz T., Bray, R. H., Anal. Chem. 24, 1640 (1952).

*[6]. Diehl, H., Ellingboe, J. L., ibid. 28, 882 (1956).

*[7]. Patton, J., Reeder, W., ibid. 28. 1026 (1956).

*[8]. Campbell, D., Kenner, C. T., Anal. Chem. 24, 560 (1954).

magnesium and calcium with Versenate method. The proposed procedure permits at the same time a good clear separation of calcium from other alkaline earths which interfere with the titration of calcium in the accurate analysis.

Apparatus and Reagents.

A cation exchange column, 1.5 sq. cm. in cross section area, was filled with the wet ammonium form of the resin to a depth of 12 cm. The resin used was Dowex 50-x8, which previously passed through 100-mesh sieve. The wet resin was transferred to the column, regenerated with 1 N solution of ammonium chloride and washed.

All reagents are analytical grade chemicals.

Indicator solution. A 0.5-gram portion of Eriochrome Black T is mixed with 4.5 grams of hydroxylamine hydrochloride and the mixture is dissolved in 100 ml. of methanol.

Standard calcium solution. Dissolve 5.0000 grams of pure calcium carbonate in dilute hydrochloric acid and dilute to one litter with distilled water. This solution contains 2.002 mg. calcium per milliliter.

Solutions of magnesium chloride, potassium and iron alums as known solutions were prepared by an appropriate volumetric or gravimetric procedure.

Standard disodium dihydrogen (ethylenedinitrilo-) tetraacetate solution. Dissolve 3.9 grams of analytical reagent material in distilled water and dilute to one liter. Standardize against the standard calcium solution using Eriochrome Black T as the indicator.

Potassium cyanide, 2 % aqueous solution

Preliminary Treatment.

A. Weigh out 0.2000 gram of finely powdered and air-dried sample into a platinum crucible (30 ml. size). Add 0.5 ml. of perchloric acid (60 %), 1 ml. of sulfuric acid (1: 1) and 5 ml. of hydrofluoric acid (40 %). Heat the partially covered crucible on a sand bath until the acids are evaporated nearly to dryness. The solution must not boil, or spattering may occur. Remove the crucible from the sand bath, cool, add 5 ml. of hydrochloric acid (1: 1) and dilute the suspension to two-thirds full of the crucible with water. Cover the crucible and heat in an air bath (crucible within a larger crucible) so that the solution boils gently. After 5 minutes of this gently boiling, the residue should be completely dissolved. Cool the solution in the crucible.

B. Weigh out 0.2000 gram of finely powdered and air-dried sample into a platinum crucible (30 ml. size), add approximately 2.0 grams of purest anhydrous sodium carbonate and mix thoroughly the sample with carbonate by rotating the crucible, then add approximately 1.0 gram of sodium carbonate on the top of the mixture. Proceed as directed in the usual procedure. Make two evaporations to dehydrate silica. Prepare the sample solution.

The volume of the solution obtained by the preliminary treatment is desirable to be 50 ml. If sufficient hydrochloric acid enough to furnish about 2 grams of ammonium chloride per 100 ml. on neutralisation is not present in the solution, add pure solid ammonium chloride to bring the concentration upto this value. Add a few drops of mentyl red indicator to the solution and precipitate the hydrous oxides by carefully adding pure ammonium hydroxide (1: 1) to the hot solution until the color of the surpernate turns to yellow and centrifuge it. Wash the precipitate with two 10-ml. portions of hot 2 % ammonium chloride solution made alkaline to methyl red with ammonium hydroxide. The volume of the resulting supernate and washings should be less than 100 ml. Transfer the solution with washing to a dropping funnel placed in position above the resin column described above, allow it to flow through the resin at a flow rate of 1 cm. per minute and wash with two 10-ml. portions of 2 % ammonium chloride.

Elution and Determination.

Elution. First, elute magnesium with 130 ml. of 1.0 N ammonium chloride eluent (exclussive of the effluent from zero to 60 ml.) at a flow of 1 cm. per minute. Collect 70 ml. of effluent containing magnesium alone in a 100-ml. volumetric flask, dilute to the mark with distilled water and reserve for the determination of magnesium. Next, elute calcium with 70 ml. of 1.6 N ammonium chloride solution containing 3 % ammonium acetate. Collect all the effluent in the same way as in the magnesium elution. Reserve the sample solution of calcium (100 ml. by volume) for determination.

Determination. Pipet duplicate aliquots (25 ml.) of the sample solution into a small beaker, add 10-ml. portion of ammonium hydroxide (1: 1) to the beaker and determine the magnesium and calcium contents by usual Versenate method using Eriochrome Black T as the indicator.

Result and Discussion.

Distribution Coefficient. The degree of the separation of two cations depends upon the difference in their distribution coefficients. The distribution coefficients of magnesium and calcium (Kd^{Mg}, Kd^{Ca}) and their ratios (Kd^{Ca}/Kd^{Mg}) were measured, some ammonium salts being used as eluent with various concentrations which are varied from 0.8 to 1.6 N. Some typical results obtained by a column method are presented in Table 1. An increase in the concentration of the salts causes a proportional decrease in the Kd's of magnesium and calcium, as is illustrated in Fig. 1. From these data a solution of less than 1.2 N ammonium chloride is recommended as the eluent for magnesium.

Table 1. Distribution coefficients of magnesium and calcium

Eluting reagent (moles)	Ammonium chloride			Ammonium acetate		
	Kd^{Mg}	Kd^{Ca}	Kd^{Ca}/Kd^{Mg}	Kd^{Mg}	Kd^{Ca}	Kd^{Ca}/Kd^{Mg}
0.6				22.4	52.5	2.34
0.8	21.6	50.7	2.43	12.5	28.0	2.24
1.0	14.5	33.0	2.27	8.3	17.1	2.06
1.2	11.3	25.6	2.26	6.1	12.0	1.95
1.4	9.8	21.9	2.24	4.6	8.5	1.85
1.6	7.2	15.1	2.10			

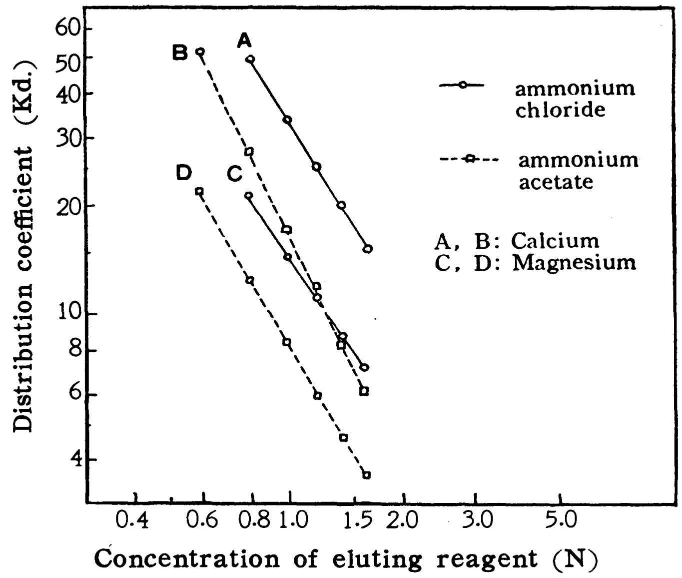

Fig. 1. Distribution coefficients of magnesium and calcium.

Elution. Elutions were all performed at room temperature with 1 N ammonium chloride for magnesium and 1.6 N ammonium chloride containing 3 % ammonium acetate for calcium at a flow rate of 1 cm. per minute. Known mixture samples were introduced into the column designated with a minimum amount of washing. Separate 5-ml. portions of effluents were collected by a fraction collector and the cation in each portion was determined by the Versenate method. An elution curve was presented in Fig. 2-a, where the known sample absorbed on the column consisted of each 0.2 meq. of magnesium and calcium. Fig. 2-b shows elution curves where the mixtures are dissolved in 100 ml. of 2 and 3 % ammonium chloride solutions, respectively. From these graphs the addition of salt to the sample solution causes to shift the elution peak to the left and to extend the range of effluent volume for magnesium. For calcium the variation in the salt concentration of sample solution has little effect on the position of the peak of elution curve, but the range of effluent volume is extended.

Table 2 shows the range of effluent volume in which cation was determined and the fraction size in which each cation was separately eluted. Furthermore, in order to investigate the effect of the calcium and magnesium quantities in a sample solution

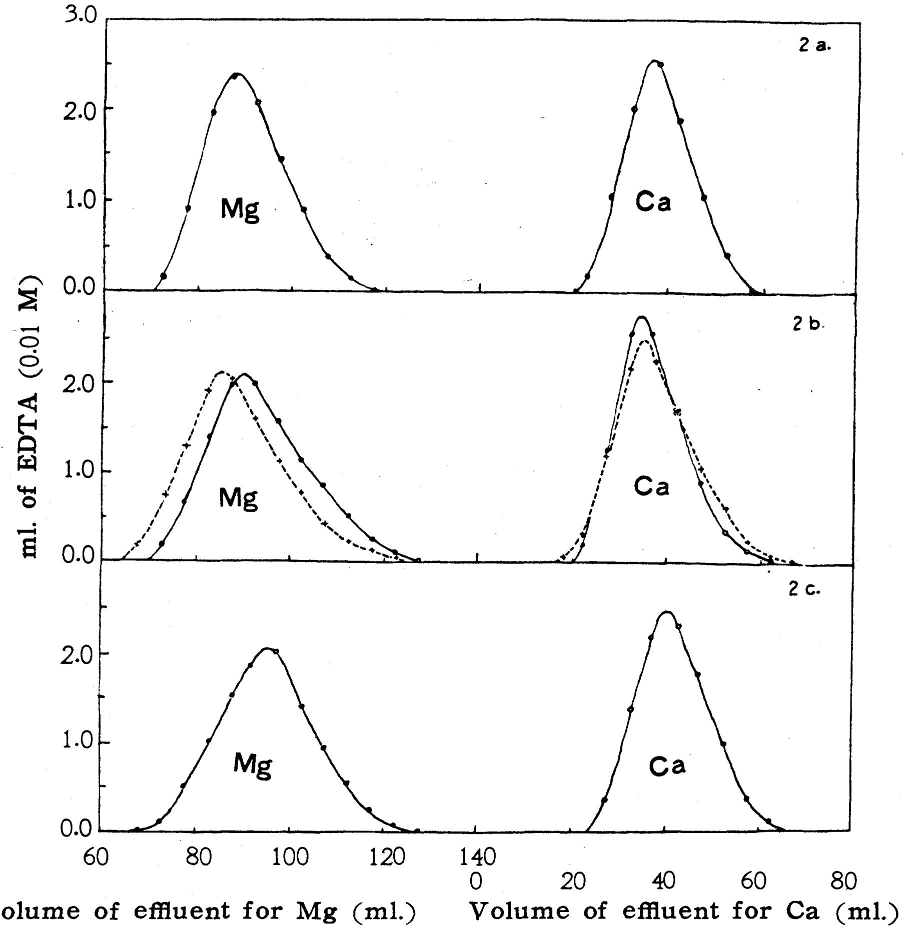

Fig. 2. Effect of concentration of ammonium chloride upon elution curve. Each mixture sample contains 0.2 meq. of Mg and Ca.
2a: the mixture sample was dissolved in 100 ml. distilled water.
2b: the mixture samples were dissolved in 100 ml. 2 % (——○——) and 3 % (——×——) ammonium chloride solution.
2c: the mixture sample was dissolved in 100 ml. of 2 % NH_4Cl solution containing 1.5 gr. of NaCl and after washing with 50 ml. of 2 % NH_4Cl solution, the elution was performed.

Table 2. The effect of salt concentration on the range of effluent volume and the fraction size

Salt concentration of sample solution (%)	Range of effluent volume in which cations were determined (ml.) Mg.	Ca.	Fraction size (ml.) Mg.	Ca.
0	70–120	20–60	50	40
1	70–120	20–60	50	40
2	70–130	20–65	60	45
3	60–130	15–70	70	55
2*	65–130	20–70	65	50

* 1.5 gram of sodium chloride is added to 100 ml. of sample solution (2 % NH_4Cl) and the resin column is washed by 50 ml. of 2 % ammonium chloride solution after introduction of the sample solution. This elution curve is shown in Fig. 2–c.

upon the range of effluent volume and the fraction size, some elutions were performed where each quantity of magnesium and calcium was varied from 0.1 to 1.0 meq. in the sample solution. Some representative results of the elution behavior are summarized in Table 3. From these experimental elutions it was found that the peak of elution curve was shifted to the left and the curve became unsymmetrical in shape as shown in Fig. 3, when the sample size became larger.

Table 3. The effected of magnesium and calcium quantities upon the elution behavior

Mixture No.	Quantity taken (meq.)		Range of effluent volume in which cations were determined (ml.)		Fraction size (ml.)	
	Mg	Ca	Mg	Ca	Mg	Ca
1	0.1	0.1	75–110	20–55	35	35
2	0.5	0.5	65–125	10–55	60	45
3	1.0	1.0	60–130	5–60	70	55
4	1.0	0.1	60–130	20–60	70	40
5	0.1	1.0	65–125	5–60	60	55

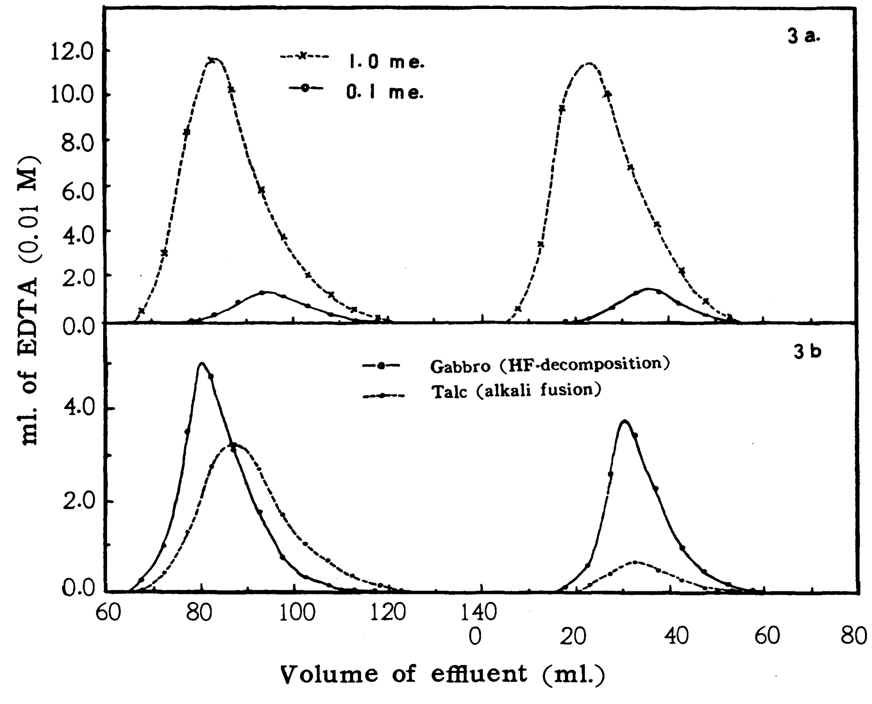

Fig. 3. Elution curves of magnesium and calcium.
3a: ---x---, shows an elution curve of a mixture sample which contained each 1.0 meq. of Mg and Ca; ——o——, for each 0.1 meq. of Mg and Ca.
3b: ——○——, and ---•--- indicate elution curves of gabbro and talc sample solutions, respectively.

In the calcium determination by Versenate method, strontium and barium which are naturally present being accompanied with calcium, are estimated as calcium without separation of these elements from calcium. These interfering ions are not simply eliminated without the ion-exchange technique and the removal of these ions was also carried out by the present procedure. Strontium is not eluted in the range of volume in which calcium is eluted, the calcium to strontium ratio being more than ten. However, where the calcium to strontium ratio is less than ten, or where the clear separation of moderate amount of calcium from strontium is required, as the eluent for calcium the methanolic solution of ammonium acetate should be used. This eluent was studied in detail elsewhere.*9

Some of the results obtained in the analysis of known salt mixtures by the recommended procedure are shown in Table 4. Each mixture contained 14.3 mg. of aluminum and 5.4 mg. of iron in addition to the indicated quantities of magnesium and calcium.

Table 4. Analysis of known mixture samples

Mixture No.	Magnesium (mg.)			Calcium (mg.)		
	Taken	Found	Error	Taken	Found	Error
1	12.72	12.70	− 0.02	20.02	20.01	− 0.01
2	1.27	1.26	− 0.01	2.00	2.03	+ 0.03
3	12.72	12.73	+ 0.01	2.00	1.99	− 0.01
4	1.27	1.28	+ 0.01	20.02	20.02	0.00

Table 5 shows the results obtained by the present method in the analysis of some silicate rocks. Samples of silicates were all decomposed by hydrofluoric and perchloric acids, and the alkali fusion method was also applied to gabbro and garnet. About 2.5 hours are required on the average for elution (flow rate 1 cm. per minute) from the time of introduction of sample solution into the column until the completion of calcium elution. However, very little of the analyst's attention is required during this period.

Table 5. Comparison of the present method and the ordinary method

Materials	By ordinary precipitation method (%)		By the present method (%)	
	MgO	CaO	MgO	CaO
Gabbro	11.27	9.03	11.26	9.05
Sea sand	2.97	3.52	2.95	3.50
Garnet	0.12	31.88	0.14	31.88
Boring core*	1.72	1.96	1.72	1.98

* from a well of natural gas.

Summary

An accurate method for the separation and determination of magnesium and calcium by employing an ion exchange column is described. The distribution

---

*9. This journal. Series I, Vol. 3, No. 2, 103 (1962) coefficients of magnesium and calcium were determined with respect to ammonium chloride and acetate. The effects of some variables such as concentration of eluent are described. The ion exchange separation of magnesium from calcium with the absence of tedious precipitating operation was found to be applicable to the determination of these elements in silicates as well as carbonates. Since this is a direct method, the accuracy with which magnesium determination is carried out, is quite satisfactory for materials which are low in magnesium and high in calcium, and the calcium determination is not interfered with other alkaline earths.