

ION EXCHANGE CHROMATOGRAPHY OF IRON, ALUMINIUM, CALCIUM AND MAGNESIUM

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A method has been worked out for the rapid determination of iron, aluminium, calcium and magnesium in ores and minerals. After the removal of silica in the usual way, the mixture in concentrated hydrochloric acid is added to an anion exchanger and eluted with the concentrated acid to remove aluminium, calcium and magnesium. Finally, iron is eluted with dilute hydrochloric acid. The mixture of the three cations (Al^{+++} , Ca^{++} , Mg^{++}) is then absorbed in a cation exchanger and successfully eluted with hydrochloric acid in the order of Mg^{++} , Ca^{++} , Al^{++} . Usual volumetric and colorimetric determinations are made on the separated ions.

Introduction

Ion exchange chromatography has been applied by others¹ to the determination of calcium and magnesium in samples like limestones and dolomite. In the present investigation, a separation technique has been worked out for the chromatography of iron, aluminium, calcium and magnesium, as these four elements are most often determined in the analysis of silicate rocks and minerals. This technique is simple and quick.

Apparatus and Reagents

A borosilicate glass column 1.8 cm. in diameter, 40 cm. high, provided with a sintered glass plate of coarse porosity was filled up with the resin up to a height of 15 cm.

Filter photometer: Hilger H 810.301.

Ion exchange resins: (a) Amberlite CG 400 (Cl^-), 100 to 200 B.S. Sieve mesh, anion exchanger in the chloride form, and (b) Amberlite CG 120 (Na^+), 100-200 B.S. Sieve mesh, a cation exchanger in the sodium form. These resins were prepared by repeatedly mixing the dry form with water and decanting after settling. The properly soaked resin was treated with 100 ml. of 3 M HCl to reactivate the exchangeable Cl^- and replace Na^+ with H^+ of the acid, transferred to the column and further washed with 100 ml. of the acid and finally several times with distilled water.

Standard solution of iron: Approximately 10 g. of $FeCl_3 \cdot 6H_2O$ were dissolved in a few ml. of hydrochloric acid. The solution was diluted to 250 ml. and standardized volumetrically: 1 ml. of the solution = 6.43 mg. of Fe^{+++} .

Standard solution of magnesium: One g. of magnesium oxide was dissolved in dilute hydrochloric acid and the solution was evaporated to dryness. The residue was taken up in water and diluted to one litre. An aliquot of this solution was standardized against E.D.T.A.: 1 ml. of the solution = 0.55 mg. of Mg^{++} .

Standard solution of calcium: One g. of calcium carbonate was dissolved in dilute hydrochloric acid and the solution was evaporated to dryness. The residue was taken up in water and diluted to one litre: 1 ml. of the solution = 0.40 mg. of Ca^{++} .

Standard solution of disodium dihydrogen ethylenediamine tetraacetate 0.4%: Four g. of the reagent was dissolved in water and the solution was made to 1 litre. The solution was standardized against the standard calcium solution: 1 ml. of the solution = 0.44 mg. of Ca^{++} = 0.27 mg. of Mg^{++} .

Eriochrome Black T indicator: The indicator powder (0.4 g.) dissolved in 100 ml. of reagent grade methanol containing 2 g. of hydroxylamine hydrochloride.

Standard solution of aluminium: Approximately 0.1 g. of $AlCl_3 \cdot 6H_2O$ was dissolved in water containing a few drops of hydrochloric acid and the solution was made to 1 litre. An aliquot of the solution is standardized gravimetrically: 1 ml. of the solution = 0.011 mg. of Al^{+++} .

Ammonium aurintricarboxylate (aluminon), 0.3% aqueous solution: The solution was allowed to stand one to two days before use.

Gum arabic solution 1%: Freshly prepared.

Ammonium acetate, 3.5 M.

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Buffer solution pH 10: Ammonium chloride (67.5 g.) was dissolved in 200 ml. of water. Ammonia (570 ml., sp. gr. 0.885) was added to make up to 1 litre.

Murexide indicator: Powdered potassium sulphate (40 g.) was mixed thoroughly with 0.2 g. of murexide.

Separation of Ca and Mg from Each Other and in the Presence of an Excess of NH_4Cl

Several mixtures of calcium and magnesium in different proportions (from 4.00-10.790 mg. of calcium and from 4.00-32.200 mg. of magnesium) were diluted to 50 ml. and transferred to the cation exchanger at a flow rate of 5 ml. per minute and washed with three separate 10 ml. portions of distilled water.

Elution of Magnesium and Calcium.—The elution was conducted with 1M hydrochloric acid. All the magnesium was recovered in the first 450 ml. of the eluate. Calcium started to come from 500 ml. and was complete in 800 ml. A clear-cut separation of the two is thus possible. In the presence of an excess of ammonium chloride, there is a shifting of the curve and separation becomes less precise (Fig. 1).

Titration of Magnesium.—The solution containing magnesium fractions was neutralized by the dropwise addition of ammonium hydroxide solution. Ammoniacal buffer of pH 10 (2 to 3 ml.) was added and the solution was titrated with the standard solution of E.D.T.A. in the presence of Eriochrome Black T as indicator.

Titration of Calcium.—The solution containing calcium fractions was neutralized with 10% solution of caustic potash and 2 ml. of the same was added in excess. The solution was then titrated with the standard solution of E.D.T.A. with murexide as indicator.

Separation and Simultaneous Determination of Fe, Al, Ca and Mg

The solution containing known amounts of Fe^{+++} , Al^{+++} , Ca^{++} and Mg^{++} , was evaporated to near dryness and taken up in 10 to 12 N hydrochloric acid and then transferred to the column of the anion exchanger [Amberlite CG 400 (Cl^-)], and washed with 4 separate portions of 10 ml. of concentrated hydrochloric acid. The washings were combined and reserved for the determination of Al^{+++} , Ca^{++} and Mg^{++} .

Elution of Iron.—Iron was eluted from the resin with approximately 200 ml. of distilled water at a flow rate of 8 ± 2 ml. per minute and finally with 50 ml. of 3 M HCl to remove the last traces of iron which might have been retained as cation in between the pores of the resin. The eluate was collected in a 500 ml. flask and made up to volume.

Estimation of Iron.—Iron was determined volumetrically by titration with potassium dichromate and colorimetrically with ammonium thiocyanate.

TABLE I.—SEPARATION OF KNOWN SOLUTIONS OF IRON.

	Amount of iron taken	Amount of iron found volumetrically	Amount of iron by colorimetric method
1.	32.13 mg.	32.1 mg.	32.5 mg.
2.	14.00 "	13.91 "	14.25 "
3.	64.20 "	65.00 "	64.25 "
4.	32.15 "	32.40 "	32.25 "
5.	32.15 "	32.20 "	32.05 "

Adsorption of the Effluent from the Iron Separation.—After the separation of iron, the remaining cations, Al^{+++} , Ca^{++} and Mg^{++} , were received in a conical flask and evaporated almost to dryness. The acid was evaporated rather than neutralized with ammonia as in the latter case, and a large amount of foreign cation NH_4^+ was introduced which not only shifted the elution curves of Ca^{++} and Mg^{++} but also made them overlap each other (Fig. 1). The mass was taken up in water and the acidity was so adjusted as to keep Al^{+++} in solution and then transferred to the cation exchanger column at a flow rate of 5 ml./minute and washed with three separate 10 ml. portions of distilled water. The effluent was found to contain no trace of cations and thus discarded.

Elution of Magnesium.—Magnesium was eluted from the resin with approximately 400 ml. of 1 M hydrochloric acid. Eight fractions of 50 ml. each were taken and titrated with E.D.T.A., using Eriochrome Black T as indicator. The first 100 ml. of the eluate contained no magnesium and could be discarded. All the magnesium was recovered in the next 300 ml. The ninth fraction was free from both magnesium and calcium.

Elution of Calcium.—The elution was continued from above where calcium appeared at the 10th fraction. The whole of Ca^{++} was eluted

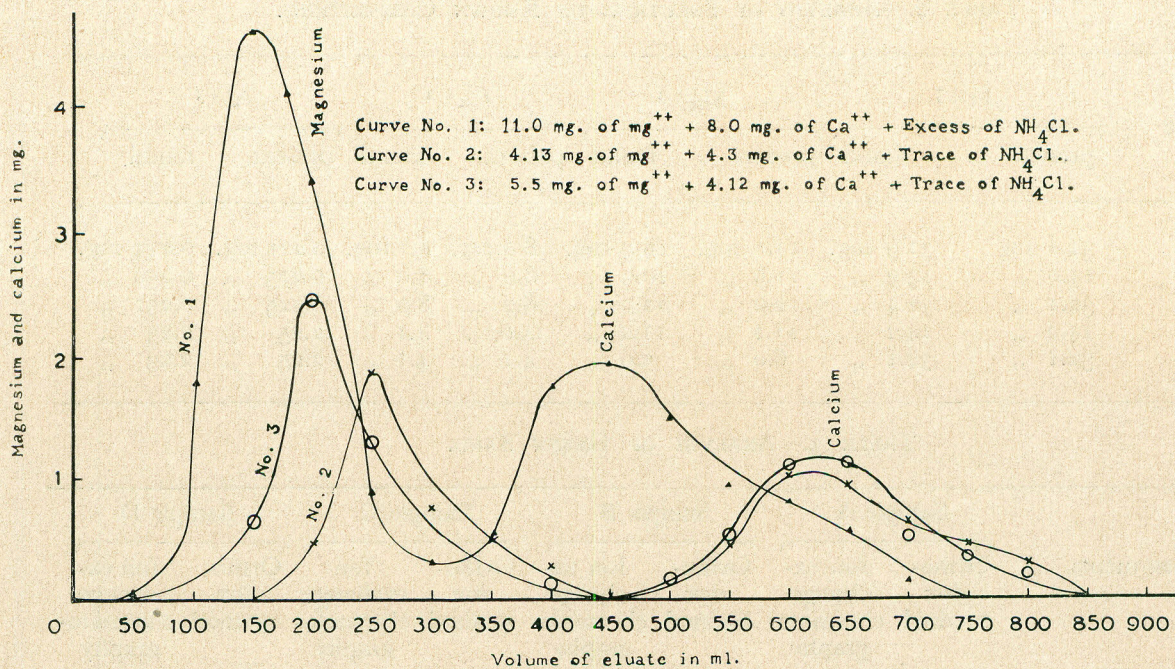


Fig. 1.—Elution curves.

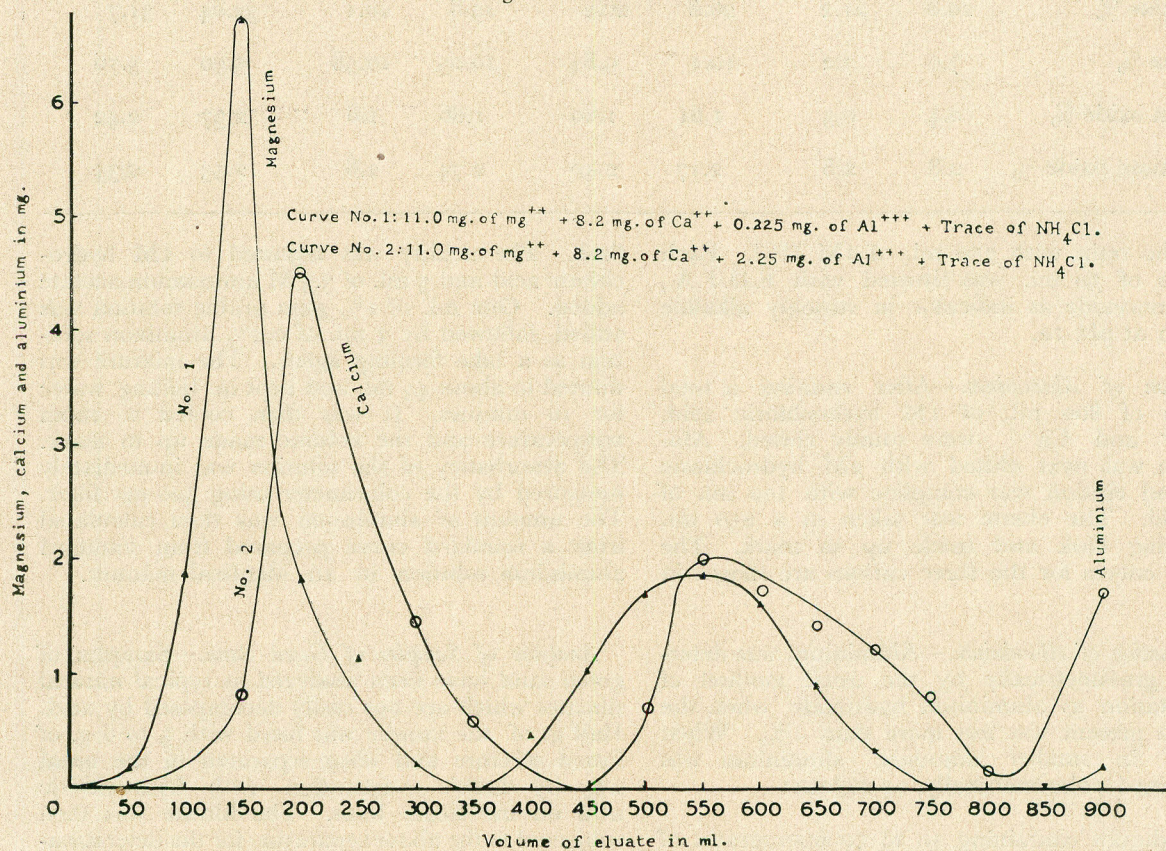


Fig. 2.—Elution curves.

TABLE 2.—ANALYSIS OF SOLUTIONS OF KNOWN COMPOSITIONS.

Sample No.	Fe ⁺³		Mg ⁺²		Ca ⁺²		Al ⁺³	
	present	found	present	found	present	found	present	found
1.	32.1 mg.	31.9 mg.	11.0 mg.	10.9 mg.	8.0 mg.	8.1 mg.	0.225 mg.	0.225 mg.
2.	14.0 „	13.9 „	11.0 „	10.9 „	8.0 „	8.0 „	0.225 „	0.250 „
3.	32.1 „	32.4 „	12.0 „	12.0 „	8.2 „	8.0 „	0.225 „	0.231 „
4.	14.0 „	14.1 „	11.1 „	11.2 „	4.0 „	4.1 „	2.25 „	2.23 „
5.	32.1 „	32.1 „	6.0 „	5.9 „	4.1 „	4.1 „	2.25 „	2.23 „

TABLE 3.—ANALYSIS OF GREEN SAND.

Constituents	Sample A		Sample B		Sample C		Sample D	
	Ortho-dox method	Ion exchange chromatography	Ortho-dox method	Ion exchange chromatography	Ortho-dox method	Ion exchange chromatography	Ortho-dox method	Ion exchange chromatography
Iron oxide %	20.8	21.2	26.8	26.2	19.6	20.1	32.04	31.7
Alumina %	7.0	7.2	10.1	9.84	10.05	10.58	5.90	5.76
Calcium oxide %	0.4	0.5	1.61	1.60	1.86	1.6	2.57	2.42
Magnesium oxide %	2.8	2.8	2.17	2.40	2.74	2.6	2.53	2.34

from the resin with 350 ml. of 1M HCl. Each fraction of 50 ml. was titrated with E.D.T.A., using murexide as indicator in strongly alkaline solution at pH 12.

Elution of Aluminium.—After running a total volume of 800 ml. of 1M hydrochloric acid, Mg⁺⁺ and Ca⁺⁺ were totally eluted. Aluminium was next eluted with 2M hydrochloric acid and elution was complete with 100 ml. of the acid. The eluate was taken in a 250 ml. measuring flask and made up to mark. The elution curves for the three cations are shown in Fig. 2.

Estimation of Aluminium.—Aluminium was determined gravimetrically by the usual method of precipitation as aluminium hydroxide when the element present was not more than 1%. When present in smaller amounts, aluminium was determined colorimetrically as follows:

An aliquot containing 10 to 20 micrograms of aluminium was transferred to a 50 ml. measuring

flask. The acidity was adjusted to 2M hydrochloric acid and 5 ml. of 3.5 M ammonium acetate added. One ml. of 1% gum arabic solution was added, followed by 3 ml. of 0.2% aluminon solution as a lake forming agent. The mixture was diluted to about 45 ml. and kept in boiling water for 10 minutes. It was then cooled to room temperature and the volume made up to mark. The absorbancy of the solution was immediately measured by the colorimeter using 520 m μ filter. The amount of aluminium was then calculated from a standard curve prepared from standard aluminium solution in an identical manner.

Analysis of Samples of Green Sand.—Samples of green sand have been analyzed as typical natural silicates which are not easily decomposed by acid. Half g. of the sample was fused with 5 to 6 g. of fusion mixture and silica separated in the usual way by double evaporation with hydrochloric acid on the steam bath. The filtrate was then subjected to the above separation for the determination of iron, aluminium, calcium and magnesium

and were estimated in the usual way. The results are shown in Table 3.

Discussion

The present work sets out in practice a method for a rapid quantitative determination of four of the common cations in most ores and minerals and specially the rocks. The sample can either be decomposed by hydrochloric acid or, if this is not possible, fused with fusion mixture and evaporated to dryness, in the usual way to remove silica. The filtrate is then subjected to the ion exchange separation, as outlined above and the results are

obtained within a few hours. The significant usefulness of the method is the removal of all difficulties of interference when one or more of the cations are estimated in the presence of others. Of special mention is the difficulty of titration of small amounts of Ca^{+2} in the presence of excess of Mg^{+2} . So is the case with the determination of aluminium in the presence of iron, calcium and magnesium.

Reference

1. C. T. Kenner, and Dan. N. Campbell, *Anal. Chem.*, **26**, 560-61 (1954).