

QUANTITATIVE INORGANIC CHROMATOGRAPHY

PART IX. THE ANALYSIS OF ALKALINE-EARTH METALS BY ION-EXCHANGE CHROMATOGRAPHY AND FLAME SPECTROPHOTOMETRY

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In a previous communication¹ a quantitative analysis of the alkaline-earth metals was described using paper chromatography and flame spectrophotometry. After the separation stage, the metals were extracted from the chromatogram and estimated by flame spectrophotometry. The use of ion-exchange chromatography avoids the extraction step necessary in the previous method.

Several workers^{2,3} have separated the alkaline-earth metals by means of cation-exchange chromatography using ammonium lactate as an eluting agent at various temperatures. The necessity for the separation of the metals when present together in a sample, has clearly been demonstrated¹ and this method allows samples containing the various alkaline-earth metals, in various concentrations, to be estimated. By use of flame spectrophotometry, a high accuracy of estimation was possible with even low concentrations.

EXPERIMENTAL

This paper describes the procedure recommended for the quantitative separation and estimation of all four alkaline-earth metals. The flame spectrophotometer used was the Unicam SP.900.

Apparatus and general technique

The cation-exchange material used for the separation was Dowex-50 W, 8%, D.V.B. cross-linked, 200-400 mesh, and the column was 66 cm long and 0.75 cm in diameter. A glass wool plug was placed at the top of the column such that when loading samples into the column, it remained undisturbed especially in its upper layers. Above the column was the usual gradient-elution system which gave the system a pressure head of about 75 cm from the top of the packed column. A Shandon automatic fraction collector (balance type) was used to collect 5.0 g samples of the eluant. Dropping rate of the column was 0.2 ml/min.

Eluting agents

Magnesium, calcium and strontium were eluted with ammonium lactate solution at pH 7.0. The first two metals were eluted using 1 M ammonium lactate, whilst the strontium was removed by gradient elution caused by dropping 3 M ammonium

lactate into 500 ml of 1M ammonium lactate in the lower reservoir (in some later samples the 3M ammonium lactate was increased to 5M lactate to decrease the elution time). Barium was removed too slowly from the column using ammonium lactate for the elution, and was eluted using 0.1M disodium ethylenediaminetetracetic acid (ENTA) buffered to pH 10.5.

The lactate solutions were prepared from the calculated quantity of AnalaR lactic acid (103 g/l for 1M solution), neutralising with 0.880 AnalaR ammonia solution to pH 7 and diluting the solution to 1 l.

The 0.1M ENTA was prepared by dissolving 37.23 g of AnalaR disodium ethylenediaminetetracetic acid in water, and adding 0.24% w/v ammonium chloride in 5N ammonium hydroxide solution until the pH 10.5 was reached. The solution was then diluted to 1 l.

Purity of water and components of eluting agents

The water used throughout this work was distilled in an all-glass apparatus having ground-glass joints. The distilled water was then passed through a mixed Zeocarb resin column about 100 cm long and 5 cm diameter contained in a hard-glass apparatus. The demineralised water was stored in hard-glass or plastic aspirators, the alkaline-earth content was below the level of detection of the flame spectrophotometer.

The alkaline-earth content of the eluting agents was found to be negligible as the eluant was diluted at least twenty-five times before determination, and the alkaline-earth metal content was below the detection limits of the spectrophotometer. However, all standard solutions of barium used in the estimations were prepared containing the appropriate concentration of ENTA because this organic component considerably enhanced the barium emission.

Solutions

(a) *Reference solutions for chromatography and flame spectrophotometry.* Standard barium solution: AnalaR barium chloride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water containing 1 mg of barium/ml.

Standard calcium solution: AnalaR calcium carbonate, CaCO_3 in 0.01N hydrochloric acid solution containing 1 mg of calcium/ml.

Standard magnesium solution: AnalaR magnesium carbonate MgCO_3 in 0.01N hydrochloric acid solution containing 1 mg of magnesium/ml.

Standard strontium solution: Strontium carbonate SrCO_3 in 0.01N hydrochloric acid solution containing 1 mg of strontium/ml.

A solution containing a mixture of 1 mg/ml of individual alkaline-earth metals was prepared from the same salts as used for the individual solutions above. These solutions were used for loading the ion-exchange column; 0.50–2.0 ml of the solution being transferred to the column.

(b) *Reference solutions for flame spectrophotometry.* The individual solutions prepared in (a) above, were then diluted to give the "working" flame spectrophotometric solutions fresh daily, the ranges were:

Calcium and strontium 0–2 $\mu\text{g/ml}$ of alkaline-earth metal.

Barium and magnesium 0–5 $\mu\text{g/ml}$ of alkaline-earth metal.

All solutions were stored in polythene screw-cap bottles.

Procedure

The resin was converted into the ammonium form by passage of approx. 3 *N* ammonium chloride solution through the resin and finally washed free of chloride ions by distilled water. The column was then "loaded" with 0.50, 1.0, or 2.0 ml of the 1 mg/ml alkaline-earth solution on to the column. The elution procedure was as follows:

(1) The lower reservoir of the gradient-elution apparatus was filled to contain 500 ml of 1 *M* ammonium lactate at pH 7.

(2) 100 ml of this solution (20 fractions) was allowed to pass through the column during which time magnesium was eluted between 65–85 ml (fractions 14–17).

(3) After step 2 was completed, the 3 *M* ammonium lactate (pH 7) was connected to the 1 *M* ammonium lactate reservoir, and gradient elution allowed to take place using the conditions of the standard practice. Calcium was eluted between a further 25–60 ml (fractions 22–29).

(4) When a further 200 ml of eluant had been collected, gradient elution was stopped. Strontium was eluted between 220–290 ml (fractions 54–60). When 5 *M* ammonium lactate was used, the strontium appeared about 60 ml (12 fractions) earlier.

(5) The column was washed with 30 ml of distilled water.

(6) The barium was eluted by passage of 50 ml of 0.1 *M* ENTA solution through the column.

Finally, 1 ml aliquots were taken from each fraction collected, diluted to a suitable concentration and estimated by flame photometry. The type of separation obtained is shown in Fig. 1. A constant eluting concentration is necessary for the sepa-

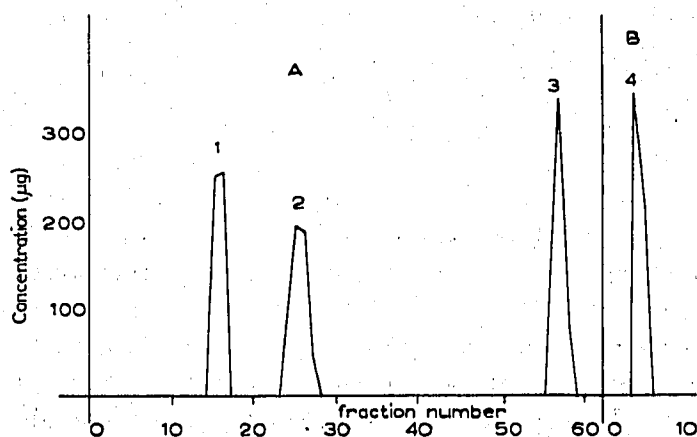


Fig. 1. Separation of alkaline-earth metals. Eluate A: ammonium lactate (pH 7). Eluate B: 0.1 *M* ENTA (pH 10.5). (1) Magnesium; (2) calcium; (3) strontium; (4) barium. 5 ml fractions.

ration of magnesium and calcium, whilst gradient elution must be employed, otherwise the strontium remains on the column too long and appears as a diffuse band. The resin is regenerated by washing with water, followed by 3 *N* ammonium chloride solution, and finally with water, after which the column is again ready for use.

Flame spectrophotometry

The instrument used was a Unicam SP.900 flame spectrophotometer operated under the following conditions:

(1) The fuel gas was B.O.G. commercial acetylene in cylinders. The cylinder

pressure must not be allowed to fall below 50 p.s.i., since there is danger of acetone (solvent for acetylene) being swept into the flame. The presence of acetone in the flame gives enhanced values for the emission of the alkaline-earth metals⁴.

(2) Atomising and oxidising gas was normal British Oxygen Company, compressed in cylinders. A cylinder was used until the pressure falls below 200 p.s.i., after which instability of the flame was noticed.

(3) The burner unit was fitted with a jet having 0.028 in. internal bore.

The operating conditions were those suggested by the manufacturers, 30 p.s.i. compressed air pressure, while the acetylene pressure varies with the need for a steady flame, but usually of the order of 3 in. measured on a dibutyl phthalate manometer. After ignition of the flame, deionized water was aspirated through the instrument which was allowed to reach thermal and electronic equilibrium. All results were recorded using the scanning motor and a Sunvic RSP 2 high speed potentiometric recorder.

The conditions used for the elements were those given in Table I.

TABLE I
SPECIAL CONDITIONS USED TO RECORD THE FLAME SPECTRA
(Electrical bandwidth: 4; photomultiplier: Mazda 27M3)

	<i>Magnesium</i>	<i>Calcium</i>	<i>Strontium</i>	<i>Barium</i>
Slit (mm)	0.08	0.04	0.04	0.04
Wavelength scan (m μ)	284.5-286.0	420-427	457-467	554-561
Amplifier gain	4.2	4.2	4.2	3.4
Recorder F.S.D. (mV)	0-1	0-10	0-10	0-1

The amplifier gain is given only as a guide, as it will vary from day to day, and instrument to instrument. The shape of the emission peaks for calcium and strontium are symmetrical on a relatively flat baseline, whilst magnesium and barium have the shape discussed in ref.¹. It was found that by using a 0-1 mV potentiometric recorder, scanning between the wavelengths given above, and allowing the recorder to "settle" it is possible to obtain a linear calibration curve for magnesium and barium which passes through zero. This procedure eliminates with the use of "pseudo peak heights", and allows lower concentrations of magnesium and barium to be determined. Using this method it was noticed that the wavelength of maximum magnesium emission varies slightly with magnesium concentration as reported by DEAN⁵.

By reference to standard calibration graphs (prepared for each determination), the concentrations of the alkaline-earth metals in the unknowns were calculated.

Analysis of synthetic mixtures

For this work, a quaternary alkaline-earth mixture was prepared as described containing 1 mg/ml of each of the alkaline-earth metals. Separations and determinations were carried out using 0.5, 1 and 2 ml of this solution. The sensitivity and applicability of this method using small quantities of one alkaline-earth metal in the presence of a large quantity of another, was tested in the analysis of mineral samples. Results for

the analysis of synthetic alkaline-earth mixtures are given in Table II. This shows that results by this method are within 3% accuracy.

TABLE II
ANALYSIS OF SYNTHETIC ALKALINE-EARTH MIXTURES

Present (μg)				Found (μg)			
Mg	Ca	Sr	Ba	Mg	Ca	Sr	Ba
500	500	500	500	511	516	495	511
1000	1000	1000	1000	1028	1003	981	1034
1000	1000	1000	1000	973	991	1000	1018
—	1000	1000	1000	—	1023	976	1007
2000	2000	—	2000	1985	2074	—	1945
2000	2000	2000	2000	2018	2050	2057	1961

Analysis of mineral samples

Limestone. A mixture of magnesium and calcium carbonates containing 38.79% calcium and 0.421% magnesium by classical chemical methods of analysis.

About 2.5 g of limestone was dissolved in the least possible quantity of dilute hydrochloric acid and made up to 250 ml with de-ionised water. 1 ml of this solution was used for analysis.

Dolomite. A mixture of magnesium and calcium carbonates containing 31.17% calcium and 5.79% magnesium. About 5 g of dolomite was dissolved in dilute hydrochloric acid and made up to 250 ml with water and 1 ml used for analysis.

Barytes. A mixture of magnesium and calcium carbonates plus barium sulphate, containing 16.83% calcium, 0.084% magnesium and 35.39% barium. About 7.5 g were fused with 6 g anhydrous sodium carbonate for 1.5 h, leached with water,

TABLE III
ANALYSIS OF MINERALS

	Chemical analysis				Found by ion exchange and flame spectrophotometry			
	Mg	Ca	Sr	Ba	Mg	Ca	Sr	Ba
Limestone (μg)	208	19,198	—	—	212.5	19,359	—	—
(%)	0.421	38.79	—	—	0.429	39.11	—	—
Dolomite (μg)	1582	8515	—	—	1612.5	8624.7	—	—
(%)	5.79	31.17	—	—	5.90	31.55	—	—
Barytes (μg)	63	1266	—	2663	60	1233	—	2487*
(%)	—	1264	—	2658	—	1256	—	2421*
	0.084	16.83	—	35.39	0.08	16.38	—	33.04
	—	—	—	—	—	16.58	—	32.23
Celestine (μg)	—	50	18,324	386	—	64	19,676	397.5
(%)	—	0.124	45.6	0.961	—	0.159	47.47	0.989

* The low result for barium in barytes has previously been found by paper chromatography by others workers⁹.

centrifuged and the residue dissolved in a little dilute hydrochloric acid and made up to 100 ml with water. 1 ml of solution used for analysis.

Celestine. A mixture of the sulphates of calcium, strontium and barium plus calcium carbonate containing 0.124 % calcium, 45.6 % strontium and 0.961 % barium. About 1 g fused as before and made up to 25 ml. 1 ml solution used.

The results given in Table III show the versatility of the method to alkaline-earth mixtures of varying concentrations.

In progress, at present, is work to automate the flame spectrophotometric estimations, and to present the elution patterns directly upon the potentiometric recorder⁷.

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SUMMARY

An ion-exchange chromatographic procedure is described for quantitative analysis of $\mu\text{g}/\text{mg}$ amounts of barium, calcium, magnesium and strontium. After elution, the metals are determined by flame spectrophotometry.

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