QUANTITATIVE INORGANIC CHROMATOGRAPHY

PART X. THE CHROMATOGRAPHIC SEPARATION AND AUTOMATIC FLAME SPECTROPHOTOMETRIC DETERMINATION OF THE ALKALINE-EARTH METALS

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A previous communication[1] described a separation of the alkaline-earth metals by cation-exchange chromatography, and the diluted effluent fractions were estimated by flame spectrophotometry. Due to the sensitivity of the flame spectrophotometer, the dilution steps in this method were somewhat tedious, work was carried out to render this step unnecessary, and it has been found possible to trace directly the elution patterns of the separated species using the flame spectrophotometer as a column effluent detector. The possibility of developing a continuous and automatic method of analysis became apparent and the method has thus been developed which is rapid, reasonably accurate and avoids the slow stages of classical methods of analysis, and yet is suited for routine analysis.

The chromatographic technique in this method differs only slightly from the previous method[1], in that a more rapid separation of the alkaline-earth metals has been achieved, complete separation and determination may be executed in under twelve hours.

EXPERIMENTAL

The flame spectrophotometer used was a Unicam SP 900 Mark I instrument as described previously[2]. Using conventional cation-exchange chromatography techniques of gradient elution, micro- and milli-gram quantities of alkaline-earth metals were separated and their concentration in the effluent (diluted to a constant volume of water by means of a simple constant volume burette[3]) was determined by direct aspiration into the flame. The area of the elution peaks so obtained was a measure of total alkaline-earth metal concentration. The accuracy of the method was found to be within 5% at all levels.

Apparatus and general technique

The chromatographic procedure was similar to that previously recommended[1] except that the resin bed length was decreased to 60 cm, and that Dowex-50W X8, 100–200 mesh replaced the Dowex-50W X8, 200–400 mesh resin. The gradient employed throughout was obtained by dropping 5 M ammonium lactate (instead of 3 M ammonium lactate) into 1 M ammonium lactate, and the pressure head was increased

to about 50 cm height. These differences in procedure considerably curtailed the elution times, thus allowing automatic detection feasible.

A constant volume delivery burette used as shown in Fig. 1, was modified from that described by GUILT AND ROBERTSON[3]. Such a device is necessary to enable
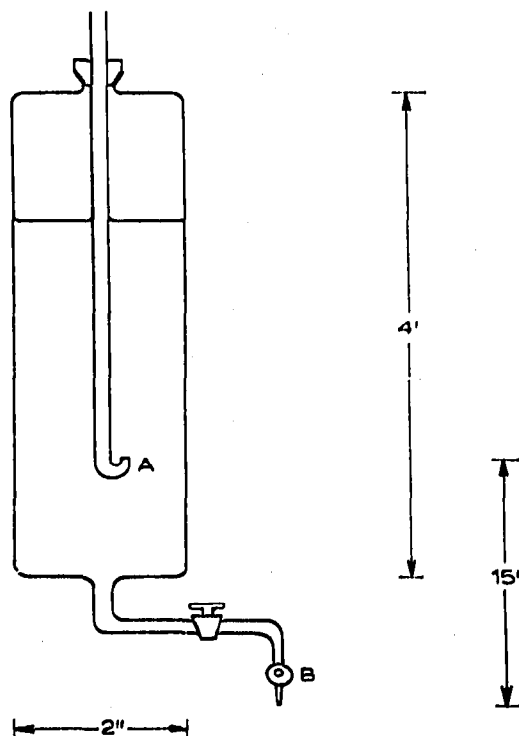

Fig. 1. Constant volume delivery burette (not to scale). A. Fine air bleed-in. B. Fine control burette tap—diaphragm type.

chromatographic elution to occur into a constant volume of solution since the column flowrate is much less than the aspiration rate of the flame spectrophotometer.

Purity of water and reagents

As in previous work, all water used was deionized and all the reagents were of AnalaR grade, the alkaline-earth content of which was negligible.

Reference solutions for chromatography

Standard barium solution	$BaCl_2 \cdot 2H_2O$ in water containing 1 mg/ml of barium.
Standard calcium solution	$CaCO_3$ in 0.01 N hydrochloric acid containing 1 mg/ml of calcium.
Standard magnesium solution	$MgCO_3$ in 0.01 N hydrochloric acid containing 1 mg/ml of magnesium.
Standard strontium solution	$SrCO_3$ in 0.01 N hydrochloric acid containing 1 mg/ml of strontium.

The column was loaded with 0.5, 1.0, and 2.0 ml aliquots of these solutions for calibration purposes.

The quantitative chromatogram

The resin was generated into the ammonium form by passage of 3 M ammonium chloride down the column followed by copious washing with water. The alkaline-earth metal bearing solutions were loaded into the column by washing on the requisite volumes of solution with distilled water. Elution was then carried out with 1 M ammonium lactate solution until the magnesium had been eluted, when after which gradient elution was started by dropping 5 M ammonium lactate solution into 500 ml of the 1 M lactate solution. Gradient elution was continued in the conventional manner until both the calcium and strontium were removed from the column. The column was then washed with water, and the barium eluted with 0.1 M disodium ethylenediaminetetraacetic acid (ENTA). Regeneration after elution, with ENTA was necessary, since it was found that the resin was converted to the sodium form, which interfered with both the sequence of the next elution, and the flame spectrophotometric estimation.

Automatic detection of the alkaline-earth metals

The column effluent was dropped into 25 ml of water kept at constant volume, which was stirred continuously. This solution was aspirated directly into the flame of the instrument, which was set at the correct wavelength to detect the alkaline-earth metal being eluted. Since the aspiration rate into the flame is greater than the flow-rate of the column, water was added from the constant volume delivery burette to keep the 25 ml of water at constant volume. In this way, the concentration of alkaline-earth metal present in the solution is directly proportional to the concentration of metal in the column effluent. By setting the flame spectrophotometer at a constant wavelength to detect the alkaline earth metal being eluted, and coupling the output of the flame spectrophotometer to a potentiometric recorder, the pattern of the eluted metal will be drawn. Under standard conditions, the area under the elution curve is proportional to the total alkaline-earth metal eluted from the column.

For the most consistent results, and the smoothest elution curves, care must be taken to observe the following points:

(a) efficient stirring of the solution aspirated into the flame;

(b) the outlets of both the ion-exchange column and the constant volume delivery burette must be just below the surface of the constant volume liquid, so that the solutions enter in a continuous stream instead of dropwise;

(c) the potentiometric recorder slightly under-damped;

(d) the dropping rate of the ion-exchange column must be constant from one run to another;

(e) the optimum wavelength for detection of each alkaline-earth metal must be found and used for maximum sensitivity and linearity of the calibration graph.

Calibration curves using 0.5 mg, 1.0 mg, 2.0 mg samples of the alkaline-earth metals were found for each element, and graphs of area *vs.* concentration were drawn.

Unknown solutions prepared from mineral samples were then eluted down the column, and the alkaline-earth content determined from the prepared calibration graphs.

Flame spectrophotometry

The SP 900 was operated under the following conditions: British Oxygen Co. cylinder

gases with 3 in. pressure of commercial acetylene, using a manometer containing dibutyl phthalate, and 30 p.s.i. of compressed air.

Unfortunately since no standards can be eluted immediately prior to determinations, the gain settings are fixed and the acetylene pressure is varied slightly from day to day to give a set deflection with a standard solution. This gives a day to day check on sensitivity and improves reproducibility of results over a period of time.

The potentiometric recorder was a Sunvic RSP. 2, 0–10 mV F.S.D., and 3 in./h chart speed.

The most critical factor affecting the estimations was the wavelength settings used for each alkaline-earth metal. Many runs were carried out using 2.0 mg of each metal to find the relationship between the peak area of the elution pattern and the wavelength of detection. These results are shown in Fig. 2; each run in this series was carried out under identical conditions. Optimum conditions are given in Table I for
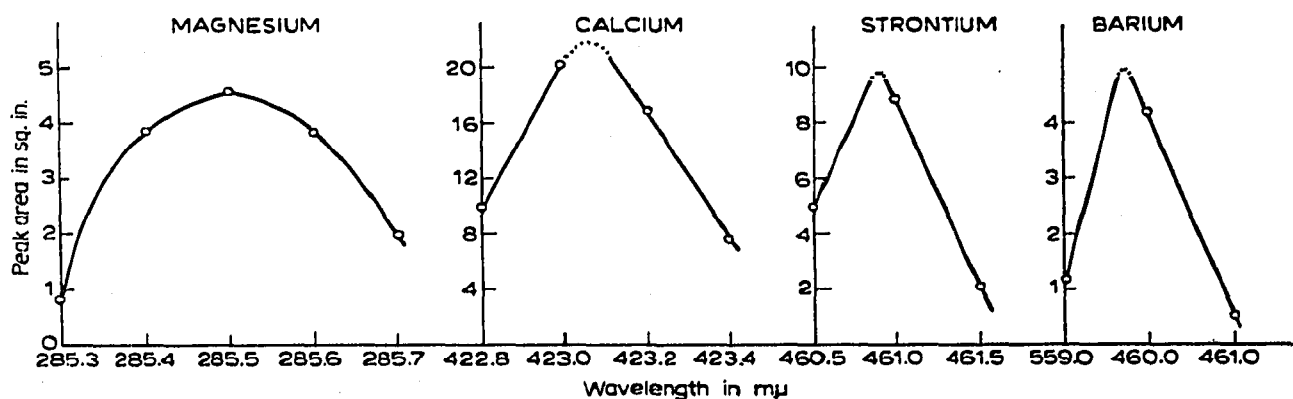

Fig. 2. Variation of peak area and wavelength for alkaline-earth metals using 2 mg samples.

each element. These settings are not absolute optimum and no doubt can be improved upon, and the used wavelength represents the optimum wavelength at which accurate location was possible.

The gain settings were kept constant, since day to day variation of the instrument was offset by variation in the acetylene pressure.

The shape of the elution patterns is given in Fig. 3. It appears from this, that the magnesium has a flattened peak, probably due to variation of maximum emission wavelength with concentration of the solution[4]. Little tailing is apparent, with barium a side peak or ledge was always noticed, and since the curve does not return to the baseline zero position, it appears that this is due to the enhancement caused by the ENTA background. In this case the peak area was taken from the base of the side peak to the tail of the peak. All areas were measured using a planimeter.

TABLE I

SPECIAL CONDITIONS USED TO RECORD THE FLAME SPECTRA

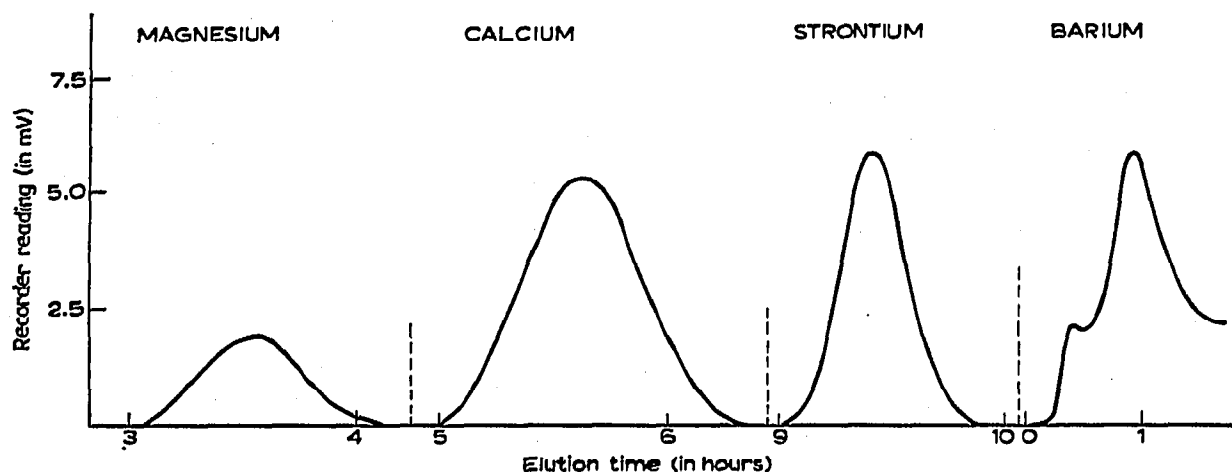| Conditions	Magnesium	Calcium	Strontium	Barium
Slit width (mm)	0.08	0.04	0.04	0.05
Wavelength (mμ)	285.5	423.0	461.0	560.0
Gain	4.0	2.2	2.2	4.5

Fig. 3. Elution curves for alkaline-earth metals. Magnesium, calcium and strontium are eluted with ammonium lactate solution, while barium is eluted with ENTA.

RESULTS AND DISCUSSION

Some results obtained for calibration are given in Table II.

These results showed that the relationship between area of elution curve and quantity of alkaline-earth metal eluted from column was linear for calcium strontium and barium, but not so for magnesium as shown in Fig. 4. The result of non-linear calibration for magnesium may be due to not setting on an optimal wavelength,

TABLE II

CALIBRATION RESULTS FOR THE ALKALINE-EARTH METALS

	Peak areas (sq. in.)											
	Magnesium			Calcium			Strontium			Barium		
Amount (mg)	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
	1.18	2.60	3.10	1.09	2.16	4.54	2.1	4.47	8.62	—	2.24	4.50
	1.12	2.40	3.00	1.16	2.15	4.70	—	4.36	9.00	—	2.21	4.25
	1.16	2.40	3.20	1.06	2.13	4.70	2.1	4.48	8.90	—	2.10	4.20
	1.23	2.53	3.25	1.07	1.92	4.52	—	4.40	8.70	—	2.25	4.25
Mean	1.15	2.48	3.14	1.10	2.09	4.44	2.1	4.43	8.81	—	2.20	4.30

but it is most likely due to the changing wavelength of maximum intensity. If the latter is the explanation, then the magnesium calibration will never be linear using such an automatic process.

The process was devised for use as a routine form of analysis which once the calibration curves are established, they can be used at any time; provided that the conditions used are standardised and are repeatable. The method should be applicable to all types of flame spectrophotometers since the constant volume of water used may be varied to enable the concentrations of the alkaline-earth metals aspirated into the flame to be altered to within the range of the instrument. Concentrations of alkaline-earth metals less than 1 mg are used; the method can be accelerated by using a shorter

column length, and a faster dropping rate, which enables all four metals to be determined in under eight hours. However, if the column length is decreased below about 55 cm, there is incomplete separation of the magnesium and calcium.
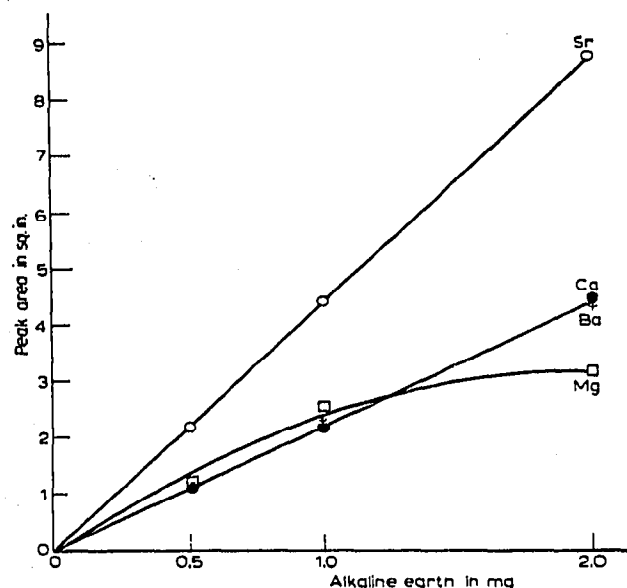

Fig. 4. Calibration curves for the alkaline-earth metals. □ magnesium; ● calcium; ○ strontium; + barium.

An indication of the applicability of this method may be judged from the analysis of some mineral samples. The results are given in Table III.

TABLE III

ANALYSIS OF MINERAL SAMPLES

		Found %	*Found previously by chromatography*[1] %	*Found by classical analysis* %
Dolomite	magnesium	5.8	5.90	5.78
	calcium	30.3	31.6	31.1
Celestine	strontium	47.3	47.5	45.6
Barytes	calcium	16.7	16.6	16.8
	barium	34.7	32.2	35.4

SUMMARY

A method of separation of microgram and milligram quantities of alkaline-earth metals using cation-exchange chromatography has been developed, using a flame spectrophotometer as a continuous automatic detector. The accuracy is within 5 %.

REFERENCES

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4 J. A. DEAN, *Flame Photometry*, McGraw-Hill, New York, 1960, p. 189.