

QUANTITATIVE INORGANIC CHROMATOGRAPHY
PART VIII. THE QUANTITATIVE ANALYSIS OF THE
ALKALINE-EARTH METALS BY PAPER CHROMATOGRAPHY
AND FLAME SPECTROPHOTOMETRY

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In a previous communication¹, a quantitative paper chromatographic separation of the alkaline-earth metals by paper chromatography was described. After separation, the metals were extracted from the paper and determined spectrophotometrically—barium, strontium and calcium with *o*-cresolphthalein complexone and magnesium with Eriochrome black T². However, although a complete but qualitative separation of the four alkaline-earth metals is described¹, no quantitative data on their separation (if all present in a mixture) was presented.

Due to the great interest shown in the previous communication¹, it was hoped that by use of paper chromatography and flame spectrophotometry, an accurate and sensitive estimation of all the alkaline-earth metals would be possible. It was decided to use flame spectrophotometry as a means of estimation, since the technique has the characteristics to enable it to be used with chromatographic procedures, that is, high accuracy at low concentrations.

The alkaline-earth metals may be determined singly, by flame spectrophotometry, with ease, but when in the presence of each other in a mixture, interference occurs. Interference covers the various effects of dissolved substances on the flame emission of the test substance. A few of these effects are understood and can be minimised, whereas others remain obscure and intricate to solve. The history and composition of every sample analysed by flame photometric techniques must receive careful examination³⁻⁶.

EXPERIMENTAL

The flame spectrophotometer used was the relatively new Unicam SP.900. Since no published work upon the effects of one alkaline earth on another using this instrument was available, an investigation of these effects was carried out. The results are described in an appendix to this paper and show how a separation of the alkaline-earth metals is desirable for results of high accuracy, about 2% at the 100 μ g level of concentration. The paper describes the procedure recommended for the quantitative separation and determination of all four alkaline-earth metals.

Apparatus and general technique

The downward elution method is used, the apparatus for which has been described by POLLARD, NICKLESS AND BANISTER⁷.

On acid-washed paper, the alkaline-earth metals are best detected by spraying with 8-hydroxyquinoline since all the metals emit a green fluorescence when held over ammonia under U.V. light. In the absence of ammonia, the fluorescence of barium and strontium spots fades rapidly, and the use of sodium rhodizonate is preferred, since the colour produced is permanent.

The detecting agents employed are: 1.0 % w/v solution of 8-hydroxyquinoline in 60 % v/v industrial methylated spirit-40 % water mixture, and a freshly prepared 0.1 % w/v aqueous solution of sodium rhodizonate.

The eluting solvents

The solvent selected was that used by POLLARD, McOMIE AND MARTIN¹—50 ml methanol, 30 ml isopropanol, 2 ml formic acid, and 2.5 g ammonium formate. The R_F values of the alkaline earths in this solvent are (10 μg of metal ion), barium 0.30, strontium 0.45, calcium 0.60, magnesium 0.75.

Purification of filter paper

The bulk of the impurities in filter paper may be extracted by soaking the paper in a dilute mineral acid. Four sheets of untreated Whatman No. 1 filter paper (25 × 56 cm) were soaked for about 5 days in 2 litres of a (1 + 5) mixture of analytical reagent concentrated hydrochloric acid and water contained in a porcelain dish (34 cm × 29 cm × 7 cm). The acid is removed by decanting, and the papers are washed with successive batches of water until the supernatant liquid fails to give a test for chloride ions with silver nitrate.

Purity of water and the components of the eluting solvent

The water used for all work, including the acid-washing of the filter-paper, was distilled in an all-glass apparatus having ground glass joints. The distilled water was then passed through a mixed Zeocarb resin column about 1 m long and 5 cm diameter held in hard-glass apparatus. The water was stored in hard-glass aspirators, the alkaline-earth content of the water was below the level of detection of the flame spectrophotometer; about 0.01 μg per ml.

The alkaline-earth content of the components of the solvent was negligible, the major error involved was the use of formic acid which contained about 2 μg of calcium per ml, but was neglected since it is present in the solvent to only 2 % amount by volume in the eluting solvent.

Solutions

(a) *Reference solutions for chromatograms.* Standard barium solution—Analytical-reagent grade barium chloride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water, containing 20 mg of barium per ml.

Standard strontium solution—Analytical-reagent grade strontium chloride $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in water, containing 20 mg of strontium per ml.

Standard calcium solution—Analytical-reagent grade calcium carbonate, CaCO_3 , was dissolved in 0.01 *N* hydrochloric acid, containing 20 mg of calcium per ml.

Standard magnesium solution—Analytical-reagent grade magnesium carbonate, MgCO_3 , was dissolved in 0.01 *N* hydrochloric acid, containing 20 mg of magnesium per ml.

From these solutions (which were standardised by normal gravimetric procedures and by flame spectrophotometric methods), a series of synthetic alkaline-earth mixtures were prepared, containing 50 μg of individual alkaline-earth metal per 0.010 ml. It was these solutions that were used for the chromatographic separations (Solutions A).

(b) *Reference solutions for flame spectrophotometry.* Solutions containing 1 mg per ml of individual alkaline-earth metals were prepared from the same salts as used in section (a) above. They also were standardised by normal gravimetric methods. These solutions were then diluted to give the "working" flame spectrophotometric solutions fresh daily, in the range 0–10 $\mu\text{g}/\text{ml}$ of alkaline-earth metal.

All solutions were stored in polythene screw-cap reagent bottles.

(c) *Solution for pilot spots of chromatograms.* A quaternary solution (Solution B) containing 10 $\mu\text{g}/3 \mu\text{l}$ of each alkaline-earth metal was also prepared for use as solution for pilot spots on some of the quantitative chromatograms.

The quantitative chromatogram

Two types of quantitative chromatogram were used, these have been described in refs.^{1,7} where the advantages and disadvantages of each were discussed in some detail.

From a calibrated Agla micrometer syringe, 0.020 ml aliquots of the solutions A containing the synthetic mixtures were delivered along the starting line. For larger volumes, the solution is put on the chromatogram in successive 0.020 ml aliquots, the chromatogram being dried at about 50° for 2–3 min between each addition. For the pilot spot chromatogram, 3 μl aliquots of solution B were used as solution for the marker spots.

The papers were air dried and placed in the chromatographic tank for 6–8 h to equilibrate. Solvent was then admitted to the trough containing the chromatogram and the paper eluted for about 12 h. As the chromatograms were eluted until the solvent front had passed the lower end of the paper, a pad of Whatman No. 1 filter paper was stapled to the lower end of the chromatogram. The pad removed the excess solvent flowing down the paper thus allowing an even solvent front to be maintained. After being dried, the metal-bearing zones are located on the quantitative chromatogram by means of the sprayed pilot strips and the bands cut out.

The zones were folded (usually in quarters) and placed in 6 in. \times 1 in. Pyrex glass test-tubes, 10.0 ml of solvent were then pipetted into each tube. The tubes were mechanically shaken for twenty minutes and left overnight for complete extraction of the alkaline-earth metals. The extracting solvent for barium, calcium, and stron-

tium was distilled water; and 1 *N* hydrochloric acid for magnesium. Blanks were prepared by extracting, with the appropriate solvent, an equal area of filter paper from a similarly eluted blank chromatogram¹.

All extracts were freed from filter paper by centrifugation (10 min maximum speed using a M.S.E. minor).

The solutions were then ready for direct aspiration into the flame spectrophotometer, except for concentration or dilution as was necessary for accurate determination.

Flame spectrophotometry

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

1. The fuel gas, 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 the acetylene) being swept over into the flame. The presence of acetone in the flame gives enhanced values for the emission of the alkaline-earth metals⁸.

2. Atomising and oxidising gas was normal B.O.G., compressed air in cylinders. A cylinder was used until the pressure falls to about 200 p.s.i., after which instability of the flame was noticed.

3. The burner unit was fitted with the larger of the two jets supplied by Unicam, having 28 thou. internal bore.

The operating conditions for the machine were those suggested by the manufacturers, about 30 p.s.i. compressed air pressure, whilst the acetylene pressure varies with the need for a steady flame usually of the order of 3 in. measured on a dibutyl phthalate manometer. After ignition of the flame, de-ionised water was aspirated through the machine 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 (0–10 mV full scale deflection).

The extracts were then aspirated into the flame and the emissions recorded. The special conditions used to record the flame spectra are given in Table I.

TABLE I
SPECIAL CONDITIONS USED TO RECORD THE FLAME SPECTRA
Electrical band width: 4. Photomultiplier: Mazda 27M3.

	<i>Magnesium</i>	<i>Calcium</i>	<i>Strontium</i>	<i>Barium</i>
Slit (mm)	0.10	0.03	0.03	0.08
Wavelength scan (m μ)	285–287	420–427	457–467	556–562
Amplifier gain	4.5	3.0	2.8	5.2

The amplifier gain is given only as a guide and will not only vary from day to day but from instrument to instrument, although the conditions above were those which gave almost a full-scale deflection on the recorder using the most concentrated solution.

The shape of the peaks for calcium and strontium is symmetrical on a relatively

flat base line (see Fig. 1a), whilst for magnesium and barium they have the shape as shown in Fig. 1b. With Fig. 1a the true base line is drawn as shown and a graph of peak height against concentration is a straight line passing through the origin. With the peak form in Fig. 1b, the peak is situated on a rapidly falling baseline. Many

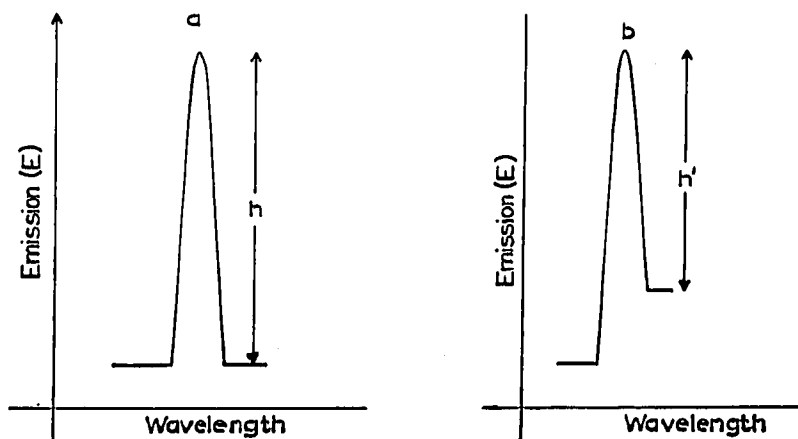


Fig. 1. Peak shapes.

constructions were tried during the investigation³ and the most reliable one found was as shown in Fig. 1b. A pseudo peak height was used, in which a base line parallel to the edge of the chart was drawn through the small minima on the low wavelength side of the main peak, the pseudo height h' vertical to this base line was measured and used. A graph of peak height h' against concentration gave a straight line which does not pass through the origin.

By reference to standard graphs (prepared for each determination) the concentration of the alkaline earths in the unknown was calculated.

Analysis of synthetic mixtures

Quaternary alkaline-earth mixtures were prepared as described above, and a few of the results are given in Table II.

TABLE II

Present (μg)				Found (μg)			
Magnesium	Calcium	Strontium	Barium	Magnesium	Calcium	Strontium	Barium
100	100	100	100	99	99	100	101
100	100	100	100	98	100	99	101

For all such chromatograms, results to within $\pm 2\%$ even down to the $50\ \mu\text{g}$ level of concentration.

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SUMMARY

A paper-chromatographic procedure is described for the quantitative analysis of microgram amounts of barium, strontium, calcium and magnesium. After separation, the metals are extracted and determined flame spectrophotometrically.

APPENDIX

 SUMMARY OF THE MUTUAL INTERACTIONS ON FLAME EMISSION
 OF PAIRS OF ALKALINE EARTHS

The results obtained are summarised in the "trend curves" in Fig. 2, where the percentage effects are shown as a function of the mole ratio of the pairs of elements

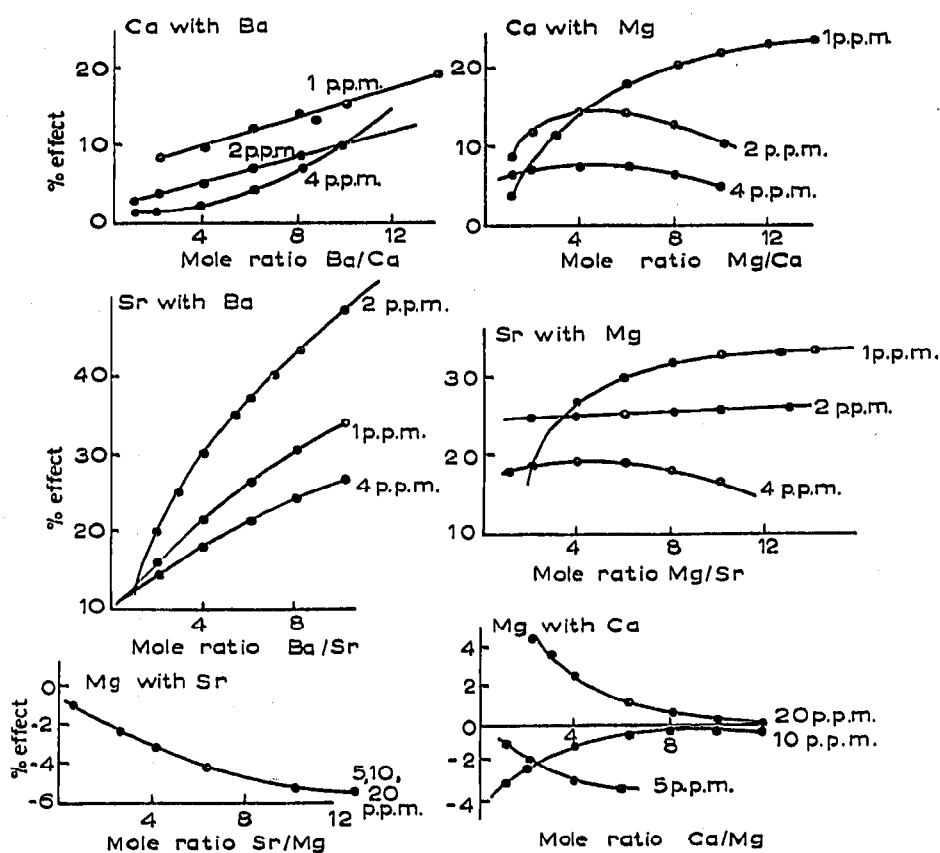


Fig. 2. Trend curves.

considered. These curves are not intended as a quantitative measure of the course of the interactions, but only as a visual aid to an evaluation of the complexity of the interactions.

Conclusions from these curves are:

- (i) (a) Calcium has no effect upon strontium up to 16:1 (at least),
- (b) Strontium has no effect upon calcium up to 16:1 (at least).

Except for the effect of calcium upon magnesium determinations, the interferences may be split into two classes:

(ii) Those showing the possibility that the foreign element may "swamp-out" its initial effects. This is seen by the magnesium interference on calcium and strontium determinations. In both cases a high concentration of magnesium leads to a fall in interference;

(iii) Those showing no manifestation of the "swamping-out" effect. The effect which is an enhancement for,

(a) barium on calcium determinations

(b) barium on strontium determinations and depressive for

(c) strontium on magnesium determinations

Appeared to increase with increase in concentration of the foreign ion.

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