Flame Photometric Determination of Alkali and Alkaline Earth Elements in Waters. II. Calcium and Strontium

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Preliminary Experiments

It is known that sodium, potassium and calcium intensify the emission of strontium while strontium has no interference with calcium[1,2,3]. In making use of this fact the writers started to elaborate a method of simultaneous determination of calcium and strontium in a solution sufficiently free from sodium and potassium in which the boundary concentration of the determinable amount, at least for strontium, is considerably lowered.

As the first step in this investigation, the writers examined in vain the possible effectiveness of additional solvents, i.e. acetone, butyl alcohol and lauryl amine hydrochloride which have proved to be very effective for

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[1] O.N. Hinsvark, S.H. Wittwer and H.M. Sell, *Anal. Chem.*, 25, 320 (1953).

[2] T.J. Chow and T.G. Thompson, *Anal. Chem.*, 27, 18 (1955).

[3] T.J. Chow and T.G. Thompson, *Anal. Chem.*, 27, 910 (1955).

the determination of sodium and potassium as reported above.

On the contrary, we found quite unexpectedly great effectiveness in oxalic acid which is used as a precipitant for separating calcium and strontium from a solution containing sodium and potassium. As suggested by these findings, other substances belonging to the same category were tested with the result that among them formic acid, acetic acid and propionic acid are found to be particularly effective. (See Table I).

TABLE I

EFFECTIVENESS OF ORGANIC ACID ON STRONTIUM EMISSION

Agent	Added amount in volume %	Intensity
Formic acid	5.0	60
	10	46
Tartaric acid	0.5	60–70
	1.0	30–35
Propionic acid	5.0	25
	10	40

Further, a comparative study of these three substances at different concentrations showed that tartaric acid especially in a 0.5% solution is the most effective of all and finally a one % solution was recommended as the best because of its greater constancy in meter reading.

On the other hand, the dependence of the intensifying effectiveness of calcium toward strontium was explored on calcium concentration with the result that strontium emission was found to increase uniformly with calcium increase (see Fig. 1).

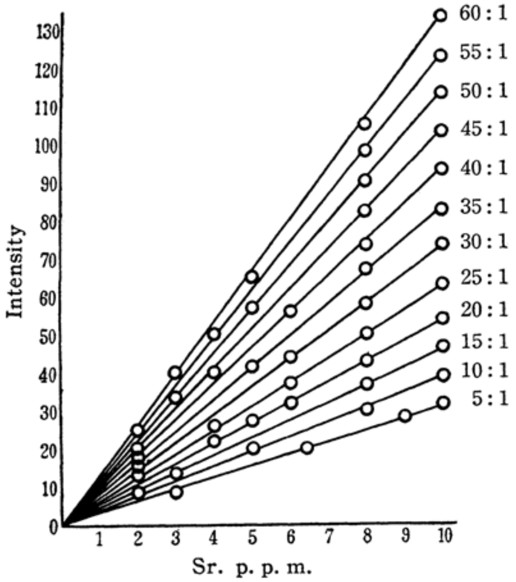

Fig. 1. Calibration curves at different Ca/Sr. Ratios on the map are Ca/Sr values for the individual curves.

Based upon these results the fundamentals of the anticipated procedure for the simultaneous determination of calcium and strontium were determined as follows: By using a precipitated mixture of oxalates of calcium and strontium with the addition of a suitable amount of tartaric acid, calcium is first determined and then after the addition of a quantity of calcium, (if necessary), the emission of strontium is determined.

Stock Solutions.—There are prepared stock solutions which contain 10% of tartaric acid, various amounts of chlorides of calcium and strontium in various proportions. Each solution is preserved in a polyethylene bottle with a cap.

Calibration Curves.—From stock solutions there are prepared several series of standard solutions as follows: A suitable amount of the stock solution is taken into a measuring flask. Suitable amounts of oxalic acid, tartaric acid and hydrochloric acid are added and the solution is made up to 500 ml. so that the final solution contains 10 ml. of hydrochloric acid (1 ; 1) and 5 g. of tartaric acid with a quantity of oxalic acid equivalent to the total of calcium and strontium. Each series of the standard solutions consists of members different in dilution but with a definite ratio Ca/Sr. For each series a calibration curve is constructed at a constant gain because of the fact that the emission of calcium itself is never influenced by the change in the amount of strontium (see Fig. 1).

Preparation of Samples.—For its lower concentration, rain water usually needs a previous concentration especially for strontium. Measured amounts, usually from 100 to 500 ml. for calcium and 1.5 to 2 liters for strontium, of the collected rain water which has passed through the pretreatment mentioned in Part I of the present paper are, if necessary, evaporated down to a volume of about 100 ml.

The next step is to prepare separate samples for determining calcium and strontium by using these condensed rain waters or any river or lake water.

To a measured amount of such a water, 2 ml. of hydrochloric acid (1 : 1), 20 ml. of a saturated solution of ammonium oxalate, 10 g. of urea and 2 drops of a methyl red solution are added successively. The solution is warmed on an electric plate until its color changes to orange-yellow.

After cooling at room temperature, the precipitate consisting of the oxalates of calcium and strontium is filtered off through a filter paper and washed five times with 10 ml. of an ammoniacal ammonium oxalate solution. With distilled water it is rinsed out into a beaker. After the addition of 2 ml. of hydrochloric acid (1 : 1), the contents of the beaker including the filter paper are warmed until thr precipitate completely dissolves. Then the solution is filtered. To the combined filtrate 2.5 ml. of a 20% tartaric acid solution is added.

TABLE II

APPLICATION TO THE SOLUTIONS WITH KNOWN AMOUNTS OF CALCIUM AND STRONTIUM

Theoretical Ca ppm	Theoretical Sr ppm	Observed Ca ppm	Observed Sr ppm	Error in ppm. Ca	Error in ppm. Sr	Error in % Ca	Error in % Sr
25	1	23.5	1.0	−1.5	0.0	−6.0	0.0
50	1	48.5	1.0	−1.5	0.0	−3.0	0.0
40	5	37.0	4.8	−3.0	−0.2	−7.5	−4.0
25	5	23.0	4.9	−2.0	−0.1	−8.0	−2.0
200	10	198.5	9.8	−2.0	−0.2	−1.0	−2.0
50	10	50.0	10.0	0.0	0.0	0.0	0.0
50	2	48.0	2.0	−2.0	0.0	−4.0	0.0
40	2	39.0	2.3	−1.0	+0.3	−2.5	+1.5
					Average	−4.0	−0.81

TABLE III

Collected on	Fraction	Sample content Ca ppm	Added Ca ppm	Theoretical Ca ppm	Found Ca ppm	Error in
July 23, '55	1	4.1	60	64.1	65.3	+1.9
	2	8.2	60	68.2	68.0	−0.29
	3	4.0	50	54.0	55.4	+2.6
	6	9.3	20	29.3	29.3	+1.7
Aug. 27, '55	2	3.5	40	43.5	42.3	−2.8
	3	7.0	40	47.0	46.0	−2.1
Sept. 7, '55	2	1.5	40	41.5	41.0	−1.2
				Average		−0.02

Collected on	Fraction	Sample content Sr ppm	Added Sr ppm	Found Sr ppm	Error in ppm	Error in %
July 23, '55	1	5.8	5	11.0	+0.2	+2
	2	4.9	5	10.0	+0.1	+1
	4	5.5	6	11.7	+0.2	+2
				Average		+2

Samples have previously been condensed down to one-sixtieth of the original volumes. Consequently, values for calcium and strontium are sixty-times greater than those in the original samples.

The solution is made up to 50 ml. and ready for flame photometry of calcium.

Samples for strontium determination are prepared as follows: To a measured amount of sample water, a suitable amount of calcium chloride solution, 2 ml. of hydrochloric acid (1:1), 20 ml. of a saturated ammonium oxalate solution, 10 g. of urea and 2 drops of a methyl red solution are added successively. Then the solution is processed as indicated for the sampls for calcium determination.

Flame Photometry.—Calcium is determined first by reading the emission intensity at about 5600 Å. Then the strontium emission is read at 4607 Å. The strontium content can be determined from the reading of the strontium emission and total calcium, calcium determined plus calcium added.

Accuracy of the Method.—The accuracy of the present method was tested in two different ways: a) The method was applied to a number of solutions containing chlorides of calcium and strontium of known composition. b) To rain water samples, the calcium or strontium content of which was previously known, certain amounts of calcium and storontium chlorides of definite concentration were added and determination was conducted.

As listed in Tables II and III, in test (a), error is from 0.0 to −8.0% with an average −4.0% for calcium and from +1.5 to −4.0% with an average −0.81% for strontium, while in test (b) it is from +2.6 to −2.8% with an average −0.02% for calcium and from +1 to +2% with an average +1.5% for strontium.

Interferences by Other Elements.—As previously mentioned, magnesium interferes considerably with both calcium and strontium. This is why we precipitate calcium and strontium in the presence of urea.

The presence of this substance secures the complete separation of calcium and strontium from magnesium. This caution is particularly essential when the method is applied to sea water.

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