700. *Qualitative Semimicro-analysis with Reference to Noyes and Bray's System : Analysis of the Combined Alkaline-earth and Alkali Groups.*

By CHRISTINA C. MILLER and ROBERT J. MAGEE.

A scheme of analysis is presented for the detection and approximate estimation of 0·1—20 mg. of barium, calcium, strontium, magnesium, sodium, lithium, potassium, rubidium, and cæsium in mixtures containing a maximum of 20 mg. of these cations in 0·4 ml. of solutions of their chlorides. In separate portions barium, magnesium, and cæsium are detected and estimated by means of potassium chromate, *p*-nitrobenzeneazoresorcinol, and potassium tetraiodobismuthate, respectively. From a fourth portion calcium is extracted by means of concentrated nitric acid and converted into calcium sulphate. Three further portions are submitted to different chromatographic separations on paper. In one, strontium is identified as its rhodizonate, in another, the fluorescent sodium and lithium zinc uranyl acetates are formed, and, in the last, the hexanitrites of potassium, rubidium, and cæsium with lead and cobalt are produced.

SCHEMES for the analysis on a semimicro-scale of nine groups of Noyes and Bray's system (" A System of Qualitative Analysis for the Rare Elements," Macmillan, New York, 1927) have already been published by Miller and Lowe (*J.*, 1940, 1258, 1263) and Miller (*J.*, 1941, 72, 786; 1943, 72; 1947, 1347). This paper describes the further application of semimicro-analytical methods to the combined alkaline-earth and alkali groups, which have already been analysed separately on a micro-scale by Benedetti-Pichler and his co-workers (*Ind. Eng. Chem.*, *Anal.*, 1939, **11**, 117; 1938, **10**, 107), whose procedures do not markedly differ from those of Noyes and Bray. Within the past decade, numerous schemes of semimicro-analysis of varying merit have been given for the alkaline-earth metals and for a group containing magnesium, potassium, and sodium, and perhaps lithium.

In Noyes and Bray's scheme the solution left after the removal of metals precipitable with ammonium sulphide may contain barium, calcium, strontium, magnesium, sodium, lithium, potassium, rubidium, cæsium, and ammonium salts, partly as perchlorates. By evaporation of the solution to dryness and moderate ignition in the presence of ammonium chloride, perchlorate is destroyed, and finally ammonium salts are eliminated. Provision can also be made for the removal of sulphate, so that eventually a solution of metal chlorides is obtained. Noyes and Bray and Benedetti-Pichler separated the metals into two groups and then systematically separated their components from one another.

Our efforts to simplify and improve the detection and estimation of the various elements by orthodox chemical methods have met with but limited success, and only for barium, magnesium, cæsium, and calcium are simple direct tests prescribed. The partition chromatographic separations on filter-paper (see preceding paper) for strontium, sodium, lithium, potassium, rubidium, and cæsium, have, however, enabled us to complete an extremely simple scheme for the detection of all the metals named, within the limits set forth in the summary.

EXPERIMENTAL.

Preparation of the Group for Analysis.—Neutral solutions containing chlorides of the various metals, and free from ammonium salts, were prepared from the purest materials obtainable.

Alkaline-earth and Alkali Groups. (The figures in parentheses are referred to in " Notes on Methods and Tests.")—*Solution* (0·4 ml.). Contains barium, magnesium, cæsium, calcium, strontium, sodium, lithium, potassium, and rubidium chlorides. Test separate portions as follows :

(*a*) Test 0·02 ml. for Ba in a fine-tapered centrifuge cone. Add 2N-acetic acid (0·02 ml.) and 3N-ammonium acetate (0·04 ml.), heat to boiling, and add *very gradually*, with continuous stirring, 1·5M-potassium chromate (0·01 ml.). A yellow precipitate shows *barium*. Reheat to b. p., cool, centrifuge, and determine (1).

(*b*) Test 0·005 ml. for Mg in a 1-ml. centrifuge cone. Add 2N-hydrochloric acid (0·05 ml.), 0·4M-calcium chloride (0·15 ml.), and 0·1% *p*-nitrobenzeneazoresorcinol in 50% ethanol (0·05—0·2 ml.). Stir well and add 2N-sodium hydroxide (0·15 ml.). Again stir, then centrifuge and wash the precipitate with water. A blue colour in the precipitate shows *magnesium*. Compare with standards and a blank (2).

(*c*) Test 0·1 ml. for Cs in a centrifuge cone (2—3 ml.). Evaporate to dryness in a current of air, cool, and dissolve the residue as far as possible in water (0·025 ml.). Add *slowly* down the side of the tube potassium tetraiodobismuthate reagent (0·05 ml.). Allow to mix, stir thoroughly, and, if the original residue has not dissolved completely, add more water (0·025 ml.). Finally, add more reagent, if required, until precipitation is complete. A brick-red, crystalline precipitate shows *cæsium*. Transfer to a fine-tapered cone for determination (3).

(*d*) Test 0·1 ml. for Ca in a centrifuge cone (2—3 ml.). Evaporate to dryness in a current of air in a heating block at 120—140°, add 0·1 ml. of nitric acid (*d* 1·42), and re-evaporate to dryness. Stir and break up the residue in more nitric acid (0·15 ml.), heat to boiling, and allow to cool. Centrifuge and repeat the extraction, if necessary. Evaporate the combined centrifugates to dryness as before, and take up the residue in water (0·08 ml.) and acetone (0·15 ml.), dissolving it as far as possible. Finally, add 0·01 ml. of concentrated sulphuric acid, stir well, and set aside for 5 minutes. If required, dissolve sulphates of metals other than calcium in more water (~0·05 ml.). A white precipitate remaining shows *calcium*. For determination, separate and wash the precipitate with acetone, then add 2N-ammonia (0·05 ml.) and 6N-ammonium carbonate (0·25 ml.). Boil for several minutes, cool, transfer to a fine-tapered cone, and compare with standards of calcium carbonate prepared *via* calcium sulphate (4).

(*e*) Test 0·01 ml. for Sr. Place the solution as a spot on a strip of Whatman No. 1 filter-paper, 1·5 cm. wide, dry, and insert the strip in a previously prepared chromatographic apparatus. Allow a mixture of hydrochloric acid (*d* 1·18) and *n*-butanol (95 : 5), saturated with *n*-butyl chloride, to travel 20 cm. down the paper from the starting line. For detection, spray with sodium rhodizonate solution. An orange- or purple-red band, one-third of the way down the paper, shows *strontium*, which is to be compared with standards (for full details see preceding paper).

(*f*) Test 0·01 ml. for Na and Li. Place the solution as a band on a strip of filter-paper, 1·5 cm. wide, dry, and insert the strip in a previously prepared chromatographic apparatus. Allow a mixture of methanol and *n*-butanol (4 : 1) to travel 20 cm. down the paper from the starting line. For detection, spray with zinc uranyl acetate reagent and examine in ultra-violet light. *Sodium* and *lithium* give fluorescent bands about one-third and two-thirds of the way down the paper, respectively, and may be determined with reference to standards (for full details, see preceding paper).

(*g*) Use two 0·02-ml. portions for K, Rb, and Cs, if test (*c*) has not been done. To one, add 0·001 ml. of 0·4M-cæsium chloride (~50 μg. of Cs). Place the solutions in bands on strips of filter paper, 4 cm. wide, and insert the latter in a previously prepared chromatographic apparatus. Allow a solvent composed of hydrochloric acid (*d* 1·18), methanol, *n*-butanol, and *iso*butyl methyl ketone (55 : 35 : 5 : 5) to reach a point 50 cm. from the starting line. For detection, use sodium lead cobalt nitrite reagent, which gives yellow bands with *potassium*, *rubidium*, and *cæsium*, the R_F values for K and Rb being ~80% and 90%, respectively, of that for Cs. Estimate by comparing with standards (full details are given in the preceding paper).

Notes on Methods and Tests.—The experimental technique has been described in earlier papers.

Note 1. This test was recommended by Noyes and Bray (*loc. cit.*) who covered a range of 0·5—500 mg. of barium in a final volume of 25 ml. Benedetti-Pichler, Crowell, and Donahoe (*Ind. Eng. Chem.*, *Anal.*, 1939, **11**, 117) used the same reaction on one-thousandth of the scale. We found it desirable, in dealing with 0·005—1 mg. of barium, to have a final volume of ~0·1 ml. In a smaller volume, the maximum amount of strontium under consideration (1 mg.) might give a slight precipitate. If desired, one may dissolve a small chromate precipitate in hydrochloric acid, evaporate to dryness, and add sodium rhodizonate to the neutral solution of the residue. Barium and strontium rhodizonate are reddish-brown, but the former is partly converted, by treatment with a small quantity of 2N-hydrochloric acid, into a very characteristic carmine precipitate, whereas strontium rhodizonate is dissolved without colour-change.

Note 2. Newell, Pike, and Ficklen (*Z. anorg. Chem.*, 1935, **225**, 281) examined the effect on this well-known test of many other cations. Alkaline-earth metals, if present in high enough concentration, might give a hydroxide precipitate, which, however, neither adsorbed the reagent with colour change nor prevented its adsorption by magnesium hydroxide. Estimations of magnesium were adversely affected by the dispersal of the blue complex in variable amounts of precipitate. The addition to all the solutions to be compared of 2 mg. of calcium ions (those most likely to be precipitated), which is far in excess of the amount that could be present in the portion of the test solution used, gave an almost constant bulk of precipitate that permitted estimations to be made and did not prevent the detection of 1 μg. of magnesium in association with any other group component (250 μg.). 0·05 Ml. of the reagent was adequate for 1—50 μg. of magnesium, but more was required for larger quantities. A trace of sulphate present in the solution, if precipitated as barium sulphate, caused the final precipitate to assume a slight colour that might be attributed to the minimum amount of magnesium. Repetition of the test in the absence of additional calcium ions prevented misinterpretation.

Note 3. Benedetti-Pichler and Bryant (*Ind. Eng. Chem.*, *Anal.*, 1938, **10**, 107) detected 5 μg. of cæsium as its iodobismuthate in the presence of 500 μg. of rubidium and potassium. Our reagent was prepared by slowly adding glacial acetic acid (25 ml.) to a suspension of bismuth oxide (1 g.) in saturated potassium iodide solution (10 ml.) (cf. Wenger, Duckert, and Rusconi, " Traité de Chimie Analytique Qualitative Minérale," Georg et Cie., Geneva, 1946, p. 284). In the prescribed test, the additional water was required to dissolve large amounts of sodium and lithium chlorides. Cæsium (25 μg.) was detectable alone and in association with any group component (5 mg.), except lithium, which raised the limit of detection to 50 μg.

Note 4. Rawson (*J. Soc. Chem. Ind.*, 1897, **16**, 113) strongly recommended the use of nitric acid (*d* 1·46) for separating soluble calcium nitrate from insoluble barium and strontium nitrates, but stated that for all ordinary purposes nitric acid (*d* 1·42) would suffice. Yagoda (*J. Amer. Chem. Soc.*, 1932, **54**, 984) used the method for separating calcium and lithium from strontium. We have found the method excellent and very simple for separating calcium from barium and strontium, even in the presence of any alkali metal or magnesium. Potassium, rubidium, cæsium, magnesium, the bulk of the lithium, and some sodium accompanied calcium. Since it was important not to dilute the nitric acid used in the extraction, the amount of water of hydration left in the mixed nitrates had to be reduced to a low level, and appreciable breakdown of magnesium nitrate into magnesium oxide, which would liberate water on reaction with nitric acid, had to be avoided. With heating between 120° and 140° there was no evidence whatever that any significant amount of barium or >5 μg. of strontium ever went into solution.

The subsequent test for calcium had to be applied in the presence of a 200-fold excess of magnesium. The test given was recommended by Shvedov (abstracted in *Analyst*, 1949, **74**, 660), who found that acetone (60—80%) hindered the precipitation of magnesium sulphate and accelerated that of calcium sulphate. In order to precipitate calcium (25 μg.) quickly, the volume of solution was kept small initially, which meant that dissolution of the mixed nitrates in aqueous acetone might be incomplete and metallic sulphates other than calcium sulphate might separate out. The addition of a minimum of water, after the sulphuric acid, cleared up the solution excellently and left the calcium sulphate. It was essential to have the metals present initially as *nitrates*. Calcium (25 μg.) could be found in association with each of the other group components (5 mg.). Calcium sulphate was unsatisfactory as a basis for estimations, but calcium carbonate sufficed, provided that the standards were also prepared from calcium sulphate precipitates.

Analysis of Mixtures.—As a final test of the validity of the proposed scheme 14 mixtures of unknown composition were submitted to the junior author for full analysis. The results shown in the table are the estimated weights (in mg.) of the metals found. Where these differed from the weights taken the latter are shown in parentheses. Cæsium was first tested for by the chromatographic procedure in order that an unbiassed decision would be made. The results obtained thus are given *first* in the table.

No.	Ba	Ca	Sr	Mg	Na	Li	K	Rb	Cs
1.	0·2	0·2 (0·1)	0	4 (2)	0	0·1	0	0·2 (0·4)	0·1, 0·2 (0·2)
2.	2 (2·4)	4 (6)	1·2	0	0	0	0·15 (0·1)	15 (10)	0, 0
3.	10 (12)	0	0·15 (0·1)	0	0	1·6 (4)	0	0·1 (0·2)	0, 0
4.	0	0·1	2 (3)	0	4 (8)	0	0·8 (1·6)	1·5 (3)	0, 0
5.	0·4 (0·8)	0·2	0	0·8 (0·4)	0	2·4	6 (8)	0·2 (0·1)	5, 12 (9)
6.	0·1	20 (16)	0·15 (0·2)	0·1	0·2 (0·4)	0·1 (0·2)	0	0	0·2, 0·8 (0·8)
7.	0	0	0	3	0·4 (0·8)	0	0	20 (16)	0, 0·1 (0·1)
8.	16	0·1	0	0·1	0·1 (0·2)	0	0	0	0·8, 0·6 (0·4)
9.	0	0·2 (0·4)	3 (9)	0	0·1 (0·1)	0·4	5	0	5, 2 (5)
10.	0·4	0	0·2	0·4 (0·8)	0	4 (8)	0·2	0	0, 0·3 (0·1)
11.	0	4	0	1·2	0·1	20 (12)	0	0·8 (1·2)	0, 0
12.	0·2 (0·1)	0·05 (0·1)	16	0·2	0	0	0·1 (0·4)	0	0, 0
13.	0·2	0	0·2 (0·4)	14 (18)	0·05 * (0)	0·1	0·1 (0·2)	0·1 (0·2)	0, 0
14.	0	0·2 (0·4)	0	12 (8)	0·15 (0·2)	8	0	0	0·1, 0·4 (0·2)

* A trace of sodium was found afterwards in the magnesium chloride solution

The results are considered satisfactory. Those obtained with reference to paper chromatograms are not inferior to results obtained otherwise. It is interesting to note that a complete analysis, including the two tests for cæsium, required $<0\cdot3$ ml. of solution. If test (*c*) for cæsium were omitted and, as suggested in the preceding paper, the detection and determination of calcium and magnesium on the same chromatogram as strontium were put on a sound basis, then the whole analysis could be done on $<0\cdot1$ ml. As a matter of interest, in the above analyses, the paper strips under examination for strontium were at the same time examined for barium, calcium, and magnesium before tests (*a*), (*b*), and (*d*) had been done. All three were correctly reported present or absent, except calcium in experiments 8 and 12, and barium in experiments 6 and 12. Loss of barium was attributed to its inadvertent precipitation as barium sulphate.

We gratefully acknowledge grants from the Trustees of the Moray Fund.

CHEMISTRY DEPARTMENT,
KING'S BUILDINGS, EDINBURGH.

[*Received, July 3rd*, 1951.]