

*The rapid separation and determination of barium, strontium, and calcium in rocks and minerals.*

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CALCIUM is one of the most widespread and abundant of metals, coming fifth on the list of elements and third among the oxides of the outer lithosphere; it is an essential constituent of a great many rock-forming minerals and is, therefore, almost always present in rocks. Barium and strontium come very much lower in the list of abundance of elements, but nevertheless barium is extremely widespread and occurs in most rocks, igneous, metamorphic, and sedimentary,<sup>1</sup> while strontium is also very widespread. It has been stated<sup>2</sup> that the average content in igneous rocks of both of these elements is of the order of 0.05%.

For many years the determination of barium, calcium, and strontium in rocks has followed well-established lines, i.e. fusion of the powdered material with sodium carbonate followed by leaching in acid, dehydration, and filtration to remove the silica. The  $R_2O_3$  group and any manganese are removed by adding an excess of ammonia and bromine water, boiling, and filtering; in the filtrate calcium, barium, and strontium are co-precipitated as oxalates and burnt off to the oxides. BaO and SrO are frequently included in the CaO result, since they occur in small amounts comparatively and the separation can only be accomplished by the difference in the solubilities of the nitrates in a mixture of absolute ether and alcohol;<sup>3</sup> this separation is not very good and must be repeated for accurate work.<sup>4</sup> It has also been stated that the strontium result is often low, as much as 18%, due to incomplete precipitation as oxalate (Groves, loc. cit., p. 59). BaO is usually determined nowadays on a separate portion by attack of the powdered mineral with a mixture of sulphuric and hydrofluoric acids followed by evaporation to dryness and the filtration and ignition of the  $BaSO_4$ . This is then fused with  $Na_2CO_3$  and leached with hot water and filtered; the residue is dissolved in dilute hydrochloric acid and a few drops of sulphuric acid added to precipitate the barium as sulphate. It must be purified from calcium by treating in a platinum crucible with concentrated sulphuric acid and heating to dissolve, when it is poured into cold water and allowed to stand overnight; under these conditions the calcium sulphate remains soluble (Groves, loc. cit., p. 138). It will thus be seen that even the determination of lime content is very lengthy, whilst the additional call for strontia or baria necessitates great time, skill, and patience.

<sup>1</sup> A. W. Groves, *Silicate analysis*. London, 1937, p. 193. [M.A. 6-483.]

<sup>2</sup> W. Noll, *Chemie der Erde*, 1934, vol. 8, pp. 507-600. [M.A. 6-87.] W. von Engelhardt, *Chemie der Erde*, 1936, vol. 10, pp. 187-246. [M.A. 6-296.]

<sup>3</sup> H. Rose, *Pogg. Ann.*, 1860, vol. 110, p. 292. W. Noll, *Zeits. Anorg. Chem.*, 1931, vol. 199, pp. 193-208. [M.A. 5-142.]

<sup>4</sup> F. P. Treadwell and W. T. Hall, *Analytical chemistry*. 9th edit., 1942, vol. 2, p. 251.

During some work on the distillation of fluorine in fluorspar by the Willard-Winter method it was noticed by the author that the sulphates of calcium and barium, both known to be present, were entirely soluble in boiling perchloric acid; this led to an investigation of the solubilities of calcium, barium, and strontium sulphates in which it was found that whilst calcium sulphate was entirely soluble in perchloric acid, both barium and strontium sulphates could be rendered insoluble, thus providing an easy method of separation from calcium. The results of this investigation were communicated to the Society of Public Analysts.<sup>1</sup> Subsequently the idea of applying this method to rocks to simplify the present tedious methods was formed and it was decided to carry out an investigation. As the method called for the use of perchloric acid it seemed obvious to try to decompose the rock by a perchloric-hydrofluoric acid mixture which would not only be much more speedy than the alkali attack but also cut out the risk of impurities in the reagents; in addition this attack would not have the disadvantage of insoluble sulphates formed in the sulphuric-hydrofluoric attack. This idea was not new: H. F. Harwood (in Groves, loc. cit., p. 137) has suggested it in a direct method for lime, but Groves (loc. cit., p. 137) found that if much lime was present there was some difficulty in decomposing the specimen completely and recommended the method chiefly for felspars. In view of this it was thought best to carry out some preliminary experiments on this method of attack, and it was found that, provided the material was sufficiently finely ground, all the rocks tried were completely attacked.

Dr. Groves kindly provided a rock sample with a lime content of 15% and this when ground to 200 mesh was entirely decomposed by the acid attack; to this specimen were added 10% additions of very refractory minerals such as ilmenite, tourmaline, and garnet, and in all cases, provided the powdering had been well carried out, complete attack was found, and the author, therefore, has no hesitation in recommending this method of attack.

After these conclusions had been reached it was reported from America<sup>2</sup> that workers there using the perchloric-hydrofluoric attack had found complete attack during their experiments and no difficulties or doubts were expressed. It was found, however, that for most rocks it was necessary to increase considerably the amount of perchloric acid and hydrofluoric acid recommended by Harwood, and this is confirmed by the American workers who more than doubled the amount. The amounts found by the author to give quick and complete attack are given below and it will be seen that these are threefold the amount recommended by Harwood, but on the other hand it has never been found necessary with this concentration to evaporate seven or eight times for a rock containing as little as 10% lime.

#### *Separation and estimation of barium.*

When considering the application of the method of separation of barium and calcium sulphate in perchloric acid to rocks, it was thought that, after the rock had been completely attacked by the perchloric-hydrofluoric acid scheme and the silica volatilized, the mere dilution with hot water and the addition of 1 ml. of sulphuric acid would be sufficient to throw out the barium as sulphate without any

<sup>1</sup> G. H. Osborn, *Analyst*, 1945, vol. 70, pp. 207-210.

<sup>2</sup> G. G. Marvin & L. B. Woolaver, *Ind. & Eng. Chem. (Anal. Edit.)*, 1945, vol. 17, pp. 554-556.

interference due to calcium; whilst if no barium were present there would be no precipitate and the absence would be seen at a glance. In point of fact these deductions proved to work very well as will be seen from the following experiments.

*Experiment 1.*—One gram of powdered rock<sup>1</sup> (< 200 mesh) containing 15% lime was weighed into a platinum crucible together with 0.1 gram BaSO<sub>4</sub> and attacked with 10 ml. HClO<sub>4</sub> and allowed to evaporate to about 5–6 ml.; then 20 ml. of HF was added and the whole evaporated to low bulk after the addition of a further 10 ml. of HClO<sub>4</sub>. When nearly taken to dryness yet a further 10 ml. of perchloric acid was added and the solution finally evaporated until salts began to crystallize. The whole was then washed into a beaker and diluted to about 150 ml. with boiling water. The solution was turbid owing to the immediate precipitation of BaSO<sub>4</sub> and 5 ml. of 1/1 sulphuric acid was added; the solution was boiled and filtered on a no. 42 Whatman, washed free of acid, burnt off, and weighed as BaSO<sub>4</sub>. The amount recovered was 0.0999 gram. The experiment was repeated exactly with the same rock powder but without the addition of barium sulphate; this time on dilution the solution remained crystal clear and the addition of sulphuric acid was without effect. It will thus be seen that the detection and estimation of barium in rocks will appear to have been much simplified, whilst its total removal makes the estimation of the calcium present much simpler at a later stage.

*The estimation of calcium as the oxalate in acetic acid.*

When considering the whole problem of the estimation of calcium in rocks and minerals, it appeared to the author that if calcium could be precipitated in acetic acid there would be no necessity to precipitate the R<sub>2</sub>O<sub>3</sub> group, and the tedious necessity of reprecipitating before the calcium could be estimated would be entirely removed. Although the author considered the insolubility of calcium oxalate in acetic acid to be a fact, a diligent search of the literature revealed no information about its application to quantitative analysis. Two German references were found,<sup>2</sup> the first qualitative and the second only semi-quantitative. There were at least two references in English,<sup>3</sup> but these were only qualitative. It was, therefore, thought advisable to carry out some experimental work to see if this method gave reasonable results and could be incorporated in the proposed scheme. Many experiments were made using very pure calcium carbonate and as a result the author feels that he has no hesitation in recommending the precipitation of calcium as the oxalate in acetic acid. The precipitation is entirely quantitative anywhere between 0.5N. and 5N. as to acid concentration, though it is very crystalline at 0.5N. and very flocculent and difficult to filter at 5N. It is, therefore, recommended that precipitation should take place from a boiling solution somewhere between 1N. and 3N. as to acid concentration. Under these conditions the

<sup>1</sup> Metamorphosed calcareous greywacke from Scotland, analysed by A. W. Groves (in M. Macgregor, Quart. Journ. Geol. Soc. London, 1937, vol. 93, p. 469): SiO<sub>2</sub> 53.91, TiO<sub>2</sub> 0.88, Al<sub>2</sub>O<sub>3</sub> 7.55, Fe<sub>2</sub>O<sub>3</sub> 0.34, FeO 3.43, MnO 0.24, MgO 2.37, CaO 15.46, BaO nil, SrO nil, Na<sub>2</sub>O 1.94, K<sub>2</sub>O 1.85, P<sub>2</sub>O<sub>5</sub> 0.77, CO<sub>2</sub> 10.30, H<sub>2</sub>O + 1.35, H<sub>2</sub>O - 0.07 = 100.46.

<sup>2</sup> K. and V. Hoffmann, Anorganische Chemie. 8th edit., 1939, p. 304. C. T. L. Neubauer and K. H. Huppert, Die Analyse des Harns. 11th edit., 1913, vol. 2, p. 1607.

<sup>3</sup> H. J. Fenton, Notes on qualitative analysis. 2nd edit., 1942, p. 21. F. P. Treadwell and W. T. Hall, Analytical chemistry. 9th edit., 1937, vol. 1, p. 262.

precipitate is crystalline and filters beautifully. No interference of any of the Fe group was detected. Typical results are given below:

Taken CaCO <sub>3</sub> (grams).	Normality.	Found CaCO <sub>3</sub> .
0.25	1	0.250
0.25	1	0.2499
0.05	$\frac{1}{2}$	0.0498
0.05	5	0.0499
0.50	2	0.501
0.50	2	0.500

With these results in mind it was decided to apply this method to the analysis of calcium in rocks and minerals, thus avoiding the precipitation and removal of the iron group.

*The direct estimation of calcium in rocks and minerals free of barium or strontium.*

If the mineral or rock for analysis is known to contain no barium or strontium then the calcium may be determined without any fusion or separation whatsoever. An example of this procedure is given below:

*Experiment 2.*—A calcium silicate (SiO<sub>2</sub> 57.3, CaO 35%, probably pectolite) was crushed very finely and a 1-gram portion weighed into a platinum crucible and attacked with 20 ml. of perchloric acid and 20 ml. of hydrofluoric acid and evaporated to dryness. It was then treated with 20 ml. of perchloric acid and 20 ml. of water and heated for a few minutes, before being washed into a beaker and diluted to 150 ml. with boiling water. The solution was crystal clear and the addition of 10 ml. 1/1 sulphuric acid produced no precipitate, showing that no barium or strontium was present. The solution was made just alkaline to litmus by ammonia from a drop bottle, 20 ml. of glacial acetic acid was added, followed after boiling a few minutes, by 25 ml. of a saturated solution of ammonium oxalate. A heavy white precipitate formed at once and after boiling and allowing to stand an hour, the solution was filtered off, washed with hot dilute acid, burnt off at high temperature, and weighed as CaO. The result, 35.56% CaO, agreed very closely with that found in duplicate by an experienced analyst using the normal fusion attack. It will thus be seen that the hydroxides of the R<sub>2</sub>O<sub>3</sub> group do not interfere; if much manganese is present a small percentage may be co-precipitated with the calcium oxalate, but this will be seen by the discoloration, and after weighing it may easily be determined either colorimetrically or volumetrically by normal methods and subtracted from the result.

*The direct estimation of calcium in rocks and minerals containing barium and/or strontium.*

In order to test the recovery by this direct method of calcium in the presence of barium and/or strontium it was decided to use a mineral free of any of these elements and to add to it varying amounts of calcium, barium, and strontium. Accordingly a sample of serpentine (H<sub>4</sub>Mg<sub>3</sub>Si<sub>2</sub>O<sub>9</sub>) was chosen and this was ground very finely and four separate portions *A, B, C, D* of 1 gram were weighed out into platinum crucibles; nothing was added to *A*, 0.1 gram of barium sulphate was added to *B*, 0.1 gram of strontium sulphate was added to *C*, while to *D* was added 0.1 gram barium sulphate and 0.1 gram calcium carbonate. To each crucible was added 20 ml. perchloric acid (60%) and 10 ml. hydrofluoric acid and the solution evaporated to dryness, when a further 20 ml. perchloric acid and 10 ml.

hydrofluoric acid were added and the solution evaporated once more to dryness. They were then treated with 20 ml. of perchloric acid, washed into a beaker and diluted to 200 ml. with boiling water, and 1 ml. of  $\text{H}_2\text{SO}_4$  added. *A* remained perfectly clear showing no barium present, *B* gave an immediate heavy precipitate indicating barium, *C* remained clear showing no barium, whilst *D* gave a heavy white precipitate indicating barium. To each was added 10 ml. of 1/1 sulphuric acid and the solutions were evaporated to 100 ml. *A* remained perfectly clear thus showing no barium or strontium, whilst *C* now gave a heavy white precipitate thus indicating strontium to be present. *B*, *C*, *D* were filtered off, washed free of acid, burnt off, and weighed. The filtrate of *D* was made just ammoniacal and then acid with 20 ml. glacial acetic and 25 ml. saturated ammonium oxalate solution added to the boiling solution; a heavy white precipitate formed which after standing an hour was filtered off, washed free of acid with boiling water and dried, burnt off, and weighed as  $\text{CaO}$ . The results found are given below:

Taken.	Found		
	$\text{BaSO}_4$ .	$\text{SrSO}_4$ .	$\text{CaCO}_3$ .
<i>A</i> , Serpentine only ... ..	nil	nil	nil
<i>B</i> , Serpentine plus 0.1 gram $\text{BaSO}_4$ ... ..	0.1005	—	—
<i>C</i> , Serpentine plus 0.1 gram $\text{SrSO}_4$ ... ..	—	0.0998	—
<i>D</i> , Serpentine plus 0.1 gram $\text{BaSO}_4$ and 0.1 gram $\text{CaCO}_3$ ... ..	0.1003	—	0.1002

It was observed that in this mineral, which contained much iron, the barium sulphate was slightly discoloured owing to iron and this doubtless accounted for the slightly higher results; this was overcome later by washing the precipitate with hot 1% hydrochloric acid.

It will thus be seen that it is possible to separate barium and strontium completely in the acid stage, and then to recover the calcium without any interference from the iron group. It will also be seen that it is possible to separate barium and/or strontium from calcium, and even to distinguish barium from strontium if either is present alone. It must be pointed out, however, that if these elements are both present the barium will co-precipitate most of the strontium on mere dilution, whilst addition of 10 ml. 1/1 sulphuric acid and evaporation to about 100 ml. will bring down all the strontium with barium. It has not yet been found possible to establish conditions where the strontium can be clearly separated from barium in perchloric acid.

In conclusion the author wishes to express his thanks to Dr. A. W. Groves and Dr. Max H. Hey for friendly discussion. Thanks are also due to the Directors of Messrs. International Alloys Ltd., Aylesbury, in whose laboratories these experiments were carried out, for permission to publish.

*Summary.*—It has been shown that provided the rock or mineral has been powdered to a sufficient fineness (e.g. 150–200 mesh) even the most refractory materials such as ilmenite, garnet, staurolite, and tourmaline may be opened up by the perchloric-hydrofluoric acid attack. It has also been shown that if barium and/or strontium are present they can be removed by simple addition of sulphuric acid and filtration, since calcium is entirely unaffected by this procedure. Finally, it has been shown that, if desired, the calcium may be extracted as oxalate in acetic acid solution without precipitation of the Fe group, and without contamination by this group.