

*The determination of rock constituents by
semi-micro-methods.*

By WINIFRED C. A. GUTHRIE, B.Sc.

and CHRISTINA C. MILLER, D.Sc.

Department of Chemistry, the University, Edinburgh.

[Communicated by Dr. F. Walker, read November 1, 1932.]

THE accurate analysis of an igneous silicate rock is a task beset with difficulties and one which, on account of the very complete analyses now required by petrologists, involves the expenditure of a considerable amount of time. The advantages which accrue from the performance of quantitative analytical operations on the micro-scale are becoming more and more apparent, and the application of at least semi-micro-analytical methods to rocks was thought to have profitable possibilities, particularly in the way of hastening the analyses. In the course of a silicate analysis there are many time-consuming operations which, if carried out on the semi-micro-scale, would be appreciably shortened, on account of the smaller volumes of liquid, and of the less bulky precipitates that would have to be handled. Publications on the analysis of rocks by micro-methods have already appeared.¹ Such methods involve the acquirement of a much more specialized technique than do semi-micro-methods.

In the following pages is given an account of the adaptation of common analytical methods to the analysis of several rocks of an average type, the amounts of material being about ten times smaller than usual. The constituents determined were silica, alumina, ferric oxide, ferrous oxide, magnesia, lime, soda, potash, water ($> 105^{\circ}$ and $< 105^{\circ}$ C.), titania, phosphorus pentoxide, and manganous oxide.

A great many preliminary experiments with standard solutions, and with artificial mixtures of quartz, alumina, ferric oxide and titania, preceded the analysis of rocks. Throughout the course of

¹ H. Hueber, *Min. Petr. Mitt.* (Tschermak), 1932, vol. 43, p. 84. [Min. Abstr., 5-238.] H. Thurnwald and A. A. Benedetti-Pichler, *Microchem.*, 1932, vol. 11, p. 200. [Min. Abstr., 5-295.]

the work W. F. Hillebrand and G. E. F. Lundell's 'Applied inorganic analysis' (1929), and H. S. Washington's 'The chemical analysis of rocks' (4th edition, 1930) were invaluable sources of reference.

Notes on Apparatus and Reagents.—A Kuhlmann micro-chemical balance of the type described in detail by Pregl¹ was used. In nearly all weighings counterpoises were used, and the time expended in taking a weighing accurate to 0.02 mg. was five minutes.

Five 6 ml. [= c.c.] platinum crucibles, 1 inch high and provided with lids, were obtained, and one was kept as a counterpoise. Small triangles of platinum wire fitted to ring supports by means of nichrome wire were used as supports for the crucibles when they were heated. Two 40 ml. palau crucibles fitted with stirrups of platinum wire served as radiators for the small crucibles during the volatilization of acids. Platinum basins of 60 ml. and 120 ml. capacity were available. Whenever possible the glass-ware used was pyrex or Jena. Several 4 ml. quartz filter crucibles proved useful.

Practically all of the reagents employed were of 'A.R.' quality, and where necessary they were carefully tested before use for non-volatile and other impurity. Hydrofluoric acid gave a negligible non-volatile residue after distillation from a platinum retort. Ammonium hydroxide was distilled at intervals and kept in a waxed Jena glass bottle. Wash solutions were invariably made up fresh when required.

(1) *Analyses of a Crinanite and an Olivine-dolerite.*—Semi-micro-methods of analysis were first applied to a crinanite and an olivine-dolerite, the analytical results for which appear, respectively, under analysis no. 329, p. 86, and analysis no. 286, p. 76, in 'Chemical analyses of igneous rocks, metamorphic rocks and minerals', a memoir published in 1931 by the Geological Survey of Great Britain. In each case part of the actual powdered sample analysed by E. G. Radley was further ground before use. As a result of many partial analyses the following procedure was found to be suitable for the determination of the rock constituents in question.

For the determination of silica, alumina, ferric oxide, titania, lime, and magnesia in the 'main portion' of rock powder, 0.1 g. was fused with 0.6 g. of sodium carbonate. The fusion cake was disintegrated with 20 ml. of water in a platinum basin, 6 ml. of 5 N hydrochloric acid were added, and the mixture was evaporated to dryness on the

¹ F. Pregl, Quantitative organic analysis, 1924, p. 7.

steam-bath. To the cold residue 1 ml. of concentrated hydrochloric acid was added, followed by 10 ml. of hot water, and the precipitate was filtered and washed with hot 5% hydrochloric acid and then with hot water. The filtrate was evaporated to dryness in order to recover a further small amount of silica. The precipitates were ignited together and corrected for impurities by volatilization with hydrofluoric acid in presence of sulphuric acid.

In the filtrate from the silica most of the acid was neutralized with 8 N ammonium hydroxide, the solution was diluted to 50 ml. and aluminium, iron, titanium, phosphorus, and any silica that escaped the first separation were precipitated with dilute ammonium hydroxide, in an almost boiling solution, according to Blum's¹ directions. Co-precipitation of manganese was brought about by the addition of 1 ml. of saturated bromine water, the liquid being kept alkaline by the simultaneous addition of dilute ammonium hydroxide. A double precipitation was done (see Washington, loc. cit., p. 173); both precipitates were thoroughly washed with a hot, neutral 2% ammonium nitrate solution. From the combined filtrates ammonium salts were expelled (Hillebrand and Lundell, loc. cit., p. 119), and a small amount of aluminium, &c., hydroxides was recovered by taking up the residue in a little hot water and rendering the solution ammoniacal. It was very important to dissolve this precipitate in acid and reprecipitate with ammonium hydroxide, for the precipitate was contaminated with calcium and alkali salts. The precipitates were ignited in a platinum crucible, and finally heated to constant weight with a blowpipe. Residual silica was determined by volatilization with hydrofluoric acid in presence of sulphuric acid, one treatment sufficing if the former was left in intimate contact with the precipitate for half an hour *before* addition of the latter. If the acids were added in the reverse way, which is more usual, complete removal of silica was not accomplished in one operation. Difficulty was experienced in obtaining constant weight after the hydrofluoric acid treatment of the precipitate, due, it was thought, to traces of moisture, derived from the hydrofluoric acid and retained by the precipitate. The remedy was found to be the addition of a little more sulphuric acid after expulsion of the acids previously added. When the usual heating had been performed a weighing was obtained which seldom changed with further blasting. Similar treatment of the ignited ammonia precipitate with a little concentrated sulphuric acid, prior

¹ W. Blum, Journ. Amer. Chem. Soc., 1916, vol. 38(2), p. 1282.

to the removal of residual silica, was also highly beneficial in expelling the last traces of moisture so that constant weight was much more readily obtained.

The precipitate was next fused with 1 g. of potassium pyrosulphate, and the melt was dissolved in 15 ml. of *N* sulphuric acid. Iron was reduced to the ferrous state with hydrogen sulphide, according to the recommendations of Lundell and Knowles,¹ platinic sulphide was filtered off, and the iron was titrated with a centinormal solution of potassium permanganate. In the titrated solution titanium was oxidized with hydrogen peroxide and determined colorimetrically.

Lime and magnesia were determined in the combined filtrates from the small 'recovered' ammonia precipitate. The acidified solution was evaporated to 10–15 ml., neutralized with ammonium hydroxide, and heated to boiling. 0.5 ml. of acetic acid and 1 ml. of a 10% oxalic solution were added, and the solution was heated and stirred for five minutes before the addition of a slight excess of 0.5 *N* ammonium hydroxide. The precipitated calcium oxalate was set aside overnight before filtration, and dissolved and reprecipitated. The precipitates were washed with 0.5 *N* ammonium hydroxide. The calcium oxalate was ignited to calcium oxide.

The combined filtrates from the calcium oxalate were acidified and evaporated to 10–15 ml. Epperson's² procedure, with appropriate diminution of the quantities of reagents, was adopted for a double precipitation of magnesium as magnesium ammonium phosphate, and its subsequent conversion to magnesium pyrophosphate.

Ferrous oxide, manganous oxide, phosphorus pentoxide, soda, potash, and water were determined in separate portions of the rocks. In the case of ferrous oxide the rock powders used by E. G. Radley were employed, not the more finely ground samples which had become partially oxidized. 0.1 g. portions were decomposed in the small platinum crucibles, according to the method described by Washington (p. 213), except that one-fifth of the usual quantities of reagents were added, and a centinormal permanganate solution was used for the titration. Manganous oxide was determined colorimetrically. 0.1 g. of rock powder was decomposed with hydrofluoric acid and sulphuric acid, heated almost to dryness, and dissolved in

¹ G. E. F. Lundell and H. B. Knowles, *Journ. Amer. Chem. Soc.*, 1921, vol. 43(2), p. 1560.

² A. W. Epperson, *Journ. Amer. Chem. Soc.*, 1928, vol. 50(1), p. 321.

5 ml. of 4 *N* sulphuric acid. Any small residue was removed and the solution was oxidized to permanganate with 0.15 g. of potassium periodate and diluted to 50 ml.

0.2 g. portions of the rocks were taken for the determination of phosphorus pentoxide as lead molybdate. Decomposition was effected in accordance with Washington's instructions (p. 247), except that one-fifth of the usual quantities of reagents were taken, and 1 ml. of a standard phosphate solution (equivalent to 0.02 g. of lead molybdate) was added to increase the amount of phosphate. Kitajima's¹ method was used in precipitating ammonium phosphomolybdate, which was then dissolved and precipitated as lead molybdate, with appropriate quantities of reagents, according to Raper's² method. The precipitate was collected in a quartz filter crucible and dried at 130°C. Experiments with standard phosphate solutions revealed that the weight of lead molybdate had to be multiplied by the factor 0.81 to give the theoretical value. Consistent results were easily obtained for the olivine-dolerite and other rock samples, but the method failed for the crinanite, no explanation of the anomaly being found.

Soda and potash were determined in 0.1 g. portions of rock powder, which were decomposed in small platinum crucibles, according to the Lawrence Smith method (Hillebrand and Lundell, p. 788). The rock was heated with 0.1 g. of resublimed ammonium chloride and 0.9 g. of precipitated calcium carbonate prepared from pure Iceland spar. The aqueous extract of the sintered cake, which contained the alkali chlorides, calcium chloride, and perhaps a little sulphate, was divided into two approximately equal portions, in one of which sodium was determined as sodium zinc uranyl acetate,³ and in the other of which potassium was determined as potassium perchlorate.⁴

For the determination of soda the solution was made slightly acid with hydrochloric acid, and evaporated to dryness in a platinum basin. The residue was dissolved in a little water, transferred to a pyrex beaker, and evaporated to 1 ml. Sodium zinc uranyl acetate was precipitated with 10 ml. of the zinc uranyl acetate reagent recommended by Barber and Kolthoff.³ If the amount of soda in the

¹ S. Kitajima, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, no. 330.

² H. S. Raper, *Biochem. Journ.*, 1914, vol. 8, p. 649.

³ H. H. Barber and I. M. Kolthoff, *Journ. Amer. Chem. Soc.*, 1928, vol. 50(1), p. 1625.

⁴ G. F. Smith and collaborators, *Journ. Amer. Chem. Soc.*, 1922, vol. 44, p. 2816; 1923, vol. 45, p. 286; 1925, vol. 47, pp. 762, 774, 1020.

rock was less than 0.5% mechanical stirring was necessary. The triple salt was filtered through a quartz crucible and washed with small quantities of the precipitating reagent, and with 95% ethyl alcohol, saturated with the triple salt. Traces of alcohol were removed in a current of air. From the weight of triple salt obtained a small amount was deducted for sodium present in the reagents.

The portion of the solution reserved for the potash determination was diluted to 40 ml., and the bulk of the calcium was precipitated as calcium carbonate by adding a little ammonium hydroxide and 0.2 g. of ammonium carbonate dissolved in water. The calcium carbonate was removed by filtration, and from the filtrate, after evaporation to dryness, ammonium salts were expelled by gentle ignition. The residue was dissolved in 3 ml. of water, and sulphate was precipitated as barium sulphate by means of a slight excess of barium chloride. After evaporation to dryness and addition of 2 ml. of water, barium sulphate was filtered off. To the filtrate in a small platinum crucible, 0.3 ml. of 60% perchloric acid was added, and the solution was evaporated to dryness, care being taken to avoid sulphate contamination. The perchlorates were extracted with a small amount of anhydrous, alcohol-free ethyl acetate, in which the solubility of potassium perchlorate is very small. Calcium, barium, and sodium perchlorates are very soluble (see Hillebrand and Lundell, p. 523). The supernatant liquid was decanted off through a dry quartz filter crucible. All of the probably slightly contaminated potassium perchlorate was dissolved in water, evaporated to dryness, and re-extracted with ethyl acetate. Again the supernatant liquid was decanted through the dry quartz filter crucible, no attempt being made to transfer the whole of the potassium perchlorate to the filter. The platinum and quartz crucibles were carefully washed with ethyl acetate, and then the perchlorate in the two crucibles was dissolved in hot water, and the solution collected in a weighed platinum crucible. After evaporation of the solution to dryness, the crucible was heated at 350°C. to constant weight. A small negative correction had to be applied to the weight of perchlorate obtained.

An attempt to determine potassium as potassium perchlorate, without prior removal of the large excess of calcium salt present after decomposition by the Lawrence Smith method, failed, unless repeated extractions with ethyl acetate were made. Precipitation of potassium as dipotassium monosodium cobaltinitrite,¹ in presence of the large

¹ M. A. Hamid, *The Analyst*, 1926, vol. 51, p. 450.

excess of calcium chloride, also failed, the precipitate being contaminated with calcium. If, however, calcium was removed from the solution, as described above, fairly satisfactory results were obtained. But they were invariably high (5–10%), and varied more amongst themselves than did results obtained by the perchlorate method. In addition, the precipitates were difficult to filter.

Decomposition of the rocks by means of hydrofluoric and sulphuric acids did not appear to offer any advantages over the method adopted.

0.1 g. portions of rock powder were used for the determination of total water according to the well-known method of Penfield.¹ Small tubes of hard glass, 12 cm. long and 5 mm. in external diameter, were used for the purpose. Rocks containing sulphur were mixed with a little freshly ignited lime prior to the expulsion of water. Values for the hygroscopic moisture in the rocks were obtained by heating 0.1 g. portions in small platinum crucibles for an hour at 105° C. These portions of rock powder could be used afterwards for the determination of manganous oxide.

In table I are given the final results of the several partial analyses made on separate portions of the crinanite and olivine-dolerite. Owing to irregularities in the weighing of the mixed oxides ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ (total iron) + $\text{TiO}_2 + \text{Mn}_3\text{O}_4 + \text{P}_2\text{O}_5$), the early determinations of silica and alumina were unsatisfactory (see p. 407), without, however, invalidating the results for ferric oxide, titania, lime, and magnesia. Silica and the mixed oxides were therefore redetermined in fresh portions of rock powder. Most of the figures given are the average of two concordant results. As no reliable results for phosphorus pentoxide were obtained for the crinanite the Survey figure was used in order to obtain the percentage of alumina. The Survey figures are appended for comparison.

On the whole the results obtained by semi-micro-methods agree quite well with the Survey results. The most obviously discordant results were those for titania and alumina in the case of the crinanite. As titania had been determined several times, in different ways, because of the discrepancy, and the percentage was invariably about 1.5, it was concluded that the lack of agreement was not due to the adoption of a semi-micro-method of analysis. The high percentage of alumina, as compared with the Survey figure, was, of course, mainly accounted for by the low value for titania. It was noted that the results for the mixed oxides tended to be high, while those for

¹ S. L. Penfield, Amer. Journ. Sci., 1894, ser. 3, vol. 48, p. 30.

TABLE I.

			Crinanite.		Olivine-dolerite.	
			Semi-micro- analysis.	Survey figures.	Semi-micro- analysis.	Survey figures.
SiO ₂	47.25	47.83	44.79	45.07
Al ₂ O ₃	17.10	15.31	14.94	14.43
Fe ₂ O ₃	1.16	1.15	1.03	0.80
FeO	9.21	9.22	10.44	10.69
MgO	6.64	6.60	14.71	14.61
CaO	12.43	12.38	9.70	9.74
Na ₂ O	2.68	2.53	1.64	1.75
K ₂ O	0.41	0.40	0.27	0.34
H ₂ O > 105° C.	1.24	1.28	1.32	1.05
H ₂ O < 105° C.	0.22	0.28	0.25	0.35
TiO ₂	1.53	2.86	0.80	0.83
P ₂ O ₅	(0.16)	0.16	0.10	0.10
MnO	0.16	0.36	0.17	0.33
Total	100.19	100.44*	100.16	100.14†
Mixed oxides‡	30.36	(30.09)	28.65	(28.37)

* Including also CO₂ 0.05, Cl 0.01, (Ni,Co)O 0.02.

† Including also BaO 0.01, CO₂ 0.02, (Ni,Co)O 0.02.

‡ Al₂O₃ + Fe₂O₃ (total iron) + TiO₂ + Mn₂O₄ + P₂O₅.

silica tended to be low. This was suggestive of incomplete removal of silica from the ignited ammonia precipitate, but the explanation could not be substantiated.

(2) *Partial analysis of a Felspar.*—‘Feldspar no. 70’ of the American Bureau of Standards was analysed according to the procedure outlined above, with the following results:

			Semi-micro-analysis.		Certificate.	
Silica	66.88 %	...	66.66 %
Mixed oxides	17.94	...	18.07

It is clear that residual silica had here been completely removed from the ignited ammonia precipitate. No doubt this was also the case with the crinanite and olivine-dolerite.

(3) *Analysis of a Plastic Clay.*—Duplicate analyses were made on two portions of ‘Plastic clay, no. 98’, of the American Bureau of Standards, for which a provisional certificate of analysis was available. According to the certificate instructions the clay was dried for two hours at 140° C. before use. The loss on ignition was found, and water was not determined. The clay contained no ferrous oxide and only a trace of manganous oxide. The minor constituents, oxides of barium, zirconium, vanadium, chromium, sulphur, and copper,

amounting in all to 0.22 %, were not determined, but barium was removed from the solution by precipitation as barium sulphate, prior to the precipitation of magnesium ammonium phosphate. The results are given in table II.

TABLE II. Plastic Clay.

	Semi-micro-analyses.		Certificate.
SiO ₂	58.98	59.15	59.10
Al ₂ O ₃	25.62	25.33	25.55
Fe ₂ O ₃	2.08	2.09	2.05
MgO	0.79	0.76	0.72
CaO	0.30	0.33	0.20
Na ₂ O	0.24	0.21	0.27
K ₂ O	3.15	3.16	3.20
TiO ₂	1.40	1.40	1.45
P ₂ O ₅	0.08	0.08	0.08
Loss on ignition	7.77	7.76	7.25
Additional constituents	(0.22)	(0.22)	0.22
Total	100.63	100.49	100.09

The duplicate analyses show excellent agreement, the deviations for all constituents, except alumina, being within the limits of permissible error given by Washington, namely, for constituents which amount to 30 % and over, 0.20–0.30 %; for those which amount to from 10 % to 30 %, 0.10–0.20 %; for those which amount to from 1 % to 10 %, 0.06–0.10 %. Moreover, the agreement with the certificate values is good, the most discordant figures being those for lime and the loss on ignition. As the amount of lime determined was minute a considerable error in the result was to be expected.

(4) *Timed Analysis of an Olivine-basalt.*—Finally, duplicate analyses were made of a sample of powdered olivine-basalt, which had been previously analysed by T. C. Day.¹ On this occasion definite working hours were adhered to, daily, in order to find the exact time required for systematic analyses.

Two analyses were started at 9 a.m. on a Monday. In the course of eight and a half hours both silica precipitates were weighed and left in contact with hydrofluoric and sulphuric acids, and soda and hygroscopic water were determined once. Contaminating salts were extracted once from a precipitate of potassium perchlorate, and the solutions for the second soda and potash determinations were made ready for evaporation. Between 9 a.m. and 5.30 p.m. on the Tuesday the main portions of silica were determined, the ammonia

¹ T. C. Day and A. G. Stenhouse, *Edinburgh Geol. Soc.*, 1930, vol. 12, p. 246.

precipitates were ignited and left in contact with hydrofluoric and sulphuric acids, potash was determined for the first time, and soda and hygroscopic water for the second time. The solution for the second potash determination was ready for treatment with perchloric acid, and one portion of rock was decomposed for the determination of manganous oxide. During the same hours on the Wednesday two determinations of manganous oxide and one of potash were made, residual silica in the mixed oxides was found, and the latter were brought into solution after fusion with potassium pyrosulphate. The calcium oxalate precipitates were ready for incineration, and precipitations of magnesium ammonium phosphate were effected. Solutions were ready for the determination of phosphorus pentoxide, and rock powder was weighed out for the ferrous oxide determinations. On the Thursday, between 9 a.m. and 6.30 p.m., lime, magnesia, titania, ferrous and ferric oxides, phosphorus pentoxide, and total water were determined, thus completing the analyses.

Two analyses, involving thirteen constituents, were therefore made in four days, three of eight and a half hours, and one of nine and a half hours, a total of 35 hours. As Washington (*loc. cit.*, p. 132) allows four days of seven to eight hours for a comparatively simple analysis on the large scale involving a dozen constituents, it is obvious that time is saved by adopting semi-micro-methods.

The speed at which the analyses were conducted did not detract from the accuracy of the results, which are shown in table III, along

TABLE III. Olivine-basalt.

	Semi-micro-analyses.		T. C. Day's analysis.
SiO ₂	44.02	43.96
Al ₂ O ₃	...	12.61	12.51
Fe ₂ O ₃	...	1.80	1.81
FeO...	...	9.67	9.70
MgO	...	12.61	12.71
CaO...	...	9.75	9.67
Na ₂ O	...	2.66	2.66
K ₂ O	...	1.61	1.63
H ₂ O > 105° C.	...	1.60	1.56
H ₂ O < 105° C.	...	0.23	0.27
TiO ₂	...	2.43	2.40
P ₂ O ₅	...	0.53	0.53
MnO	...	0.18	0.19
CO ₂	(0.07)	(0.07)
FeS ₂	(0.32)	(0.32)
Total	...	100.09	99.99
			100.34

with Mr. Day's figures. Mr. Day's figures for FeS_2 and CO_2 were used in order to give a summation in the first two columns.

In conclusion, if sufficient care be exercised in manipulation and precautions taken to prevent contamination from external sources, semi-micro-analytical methods may be applied to rocks, with no serious loss of accuracy, and with a considerable saving of time. It is noteworthy that the semi-micro-analyses were performed with simple apparatus, with a comparatively small amount of platinum, and in a laboratory with only ordinary facilities for analytical work. No evaporations were carried on overnight. The fact that thirteen constituents can be determined with 0.6–0.7 g. of rock powder might be of great advantage in specific cases; five portions each of 0.1 g. being used for the 'main portion', for alkalis, FeO , $\text{H}_2\text{O} < 105^\circ \text{C}$. and MnO , $\text{H}_2\text{O} > 105^\circ \text{C}$., and one of 0.1–0.2 g. for P_2O_5 .

We have much pleasure in acknowledging our indebtedness to Dr. F. Walker, who supplied the samples of the crinanite and olivine-dolerite, and to Dr. R. Campbell, who provided the olivine-basalt. To Sir James Walker, F.R.S., we accord our warm thanks for his constant interest, and for the encouragement he has given us throughout the course of the work. For a Carnegie Teaching Fellowship held by the senior author and for several grants from the Trustees of the Moroy Fund we are duly grateful.
