The separation of manganese in rock analysis.

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THE separation and estimation of small quantities of manganese in the course of exact analysis of igneous and metamorphic rocks has long presented a difficulty. The element is almost universally present, in amounts varying from a few hundredths of one per cent. to over one per cent., the higher figure being reached in the basic rocks, especially in those rich in ferromagnesian minerals. In the ordinary course of analysis, if no special method be adopted to separate and remove manganese, this element tends to be distributed between the 'ammonia precipitate' and the lime and magnesia. It has been shown by G. Steiger[1] that when the usual methods are employed, the manganese tends to be distributed in a quite haphazard way among the three precipitates; no definite proportion is retained by any one of them, although as a general rule most of the manganese is found with the magnesia and least with the lime. In those cases where the total amount of manganese present in the rock is small (0·1 % or less) no serious error is involved in disregarding its presence in the three precipitates, yet when larger amounts are in question, and especially in all cases where results of the highest accuracy are desirable, it is necessary to make some modification of the usual analytical procedure in order to permit of the concentration of the manganese in one particular precipitate, or, alternatively, to ascertain its distribution amongst the weighed precipitates of lime, magnesia, and alumina, so that a correction can be subsequently introduced. The present paper is an attempt to furnish a solution of this problem. Several methods have previously been suggested to achieve the above-mentioned result: they are outlined, and briefly criticized below:

1. Precipitation of the manganese by ammonium sulphide after removal of ferric oxide, alumina, &c., by means of ammonia.

[1] W. F. Hillebrand, The analysis of silicate and carbonate rocks. Bull. U.S. Geol. Survey, 1907, no. 305, p. 96.

2. Precipitation of the ferric oxide and alumina by the basic acetate method, followed by separation of the manganese as in (1) or by means of sodium acetate and bromine.

3. The manganese present in the lime and magnesia precipitates is determined colorimetrically in the solutions of the ignited and weighed precipitates. The total manganese present in the rock is determined colorimetrically in a separate weighed quantity, and the manganese which has been co-precipitated with the alumina is thus found by difference. The necessary corrections are then applied to all three precipitates.

4. Precipitation of the manganese quantitatively with the alumina precipitate, by the employment of an oxidising agent in the presence of ammonia.

The first method yields accurate results, but the removal of the manganese as sulphide is tedious, as the precipitate must stand overnight before filtration. Filtration itself is apt to be slow, and the excess of ammonium sulphide must be removed from the filtrate, so that the time required for carrying out an analysis is appreciably lengthened by these operations. Method (2) may be employed in the analysis of manganese ores, where the greatest accuracy is not required. It is not suited for use in rock analysis, as the precipitation of ferric oxide and alumina is never quite complete, especially when alumina predominates largely, as is usually the case with igneous rocks ; also if the manganese in the filtrates be precipitated by means of sodium acetate and bromine, appreciable quantities of calcium are co-precipitated. The third method involves three separate determinations of manganese, but is fairly satisfactory, apart from the expenditure of time required. Its main objections are, that no determination of strontia in the lime precipitate can be made, and it is not possible to determine the amount of calcium invariably to be found in the magnesia precipitate. There is also some doubt as to the exact condition in which the manganese is present in the ignited magnesia precipitate : manganese ammonium phosphate is unstable in ammoniacal solution of the strength necessary for precipitating the magnesium, and consequently some manganese peroxide is always formed, a precipitate of magnesia which contains manganese being coloured brownish after ignition. The fourth method appears to be the most promising, as there is no difficulty in ensuring the complete precipitation of the whole of the manganese with the alumina by the simultaneous addition of an oxidizing agent : the objection to the method in its existing forms lies in the fact that small amounts of the other bases present, especially lime, tend to be carried

down in the precipitate in the form of manganites, and these are not wholly removed even by a second precipitation.

The present paper deals with a critical examination of the various oxidizing agents suitable, and their employment under varying conditions, with the object of seeing if it might not be possible to reduce the co-precipitation of lime and magnesia to a negligible minimum, or to obviate it entirely. The investigation has been confined to solutions containing from 1 to 50 milligrams of manganese, as a method which functioned satisfactorily between the above limits would prove applicable in practically all cases of rock analysis. Of the various oxidizing agents which suggested themselves as suitable, ammonium persulphate, hydrogen peroxide, chlorine, and bromine were tried. The use of the first of these has been previously proposed in the United States Geological Survey, Bulletin no. 700 (1919, p. 111), for this purpose, and has been adopted by H. S. Washington in his book on rock analysis.[1] The experience of the present authors in regard to this method was unfavourable. It was found impossible, even by a double precipitation, to obtain the whole of the calcium in the filtrate, and the presence of the relatively large amount of sulphate introduced into the analysis is also objectionable. The second reagent, hydrogen peroxide, would be particularly satisfactory if applicable, as it does not introduce any new ions into the solution, and any excess is easily removed by boiling. An extended series of experiments, in which the peroxide was added either prior to, with, or subsequent to the ammonia showed, however, that although the precipitation of the manganese with the alumina was quantitative, the precipitate invariably contained appreciable amounts of lime which could not be removed completely even after two precipitations. The use of chlorine as oxidizing agent gave similar results : the chlorine was introduced in two ways, either in the form of sodium hypochlorite, or by boiling the acidified solution with potassium chlorate, and then neutralizing with ammonia whilst Cl_2 and ClO_2 were being evolved. The precipitation of the manganese was complete under these conditions, but in every case considerable quantities of calcium were carried down in the precipitate.

Preliminary experiments with bromine as oxidizing agent gave more promising results, and it was finally decided to investigate this method quantitatively. For this purpose a number of carefully standardized solutions of the chlorides of aluminium, iron, calcium, and magnesium were prepared. Equal volumes of these solutions were then mixed, and

[1] H. S. Washington, Manual of the chemical analysis of rocks. 3rd edition, 1919, p. 151.

portions of 25 c.c. of the resulting solution used for each experiment. The strength of the various solutions was chosen so that the final liquid would contain amounts of the constituents similar to those which would be present in the solution obtained during the analysis of an average rock ; a typical solution contained, in the form of chlorides, Al_2O_3 0·175, Fe_2O_3 0·10, CaO 0·075, MgO 0·0375 gram. The requisite amount of manganese was then added in the form of a standardized solution of manganese chloride, and the separation carried out. The precipitate of ferric oxide, alumina, and manganese oxide was filtered off, redissolved, and reprecipitated. In the united filtrates the lime and magnesia were determined by the usual methods.[1]   Both these precipitates were redissolved after being weighed, and the resulting solutions tested for manganese by the periodate method, but in no case was this element found in more than unweighable traces, and usually it was entirely absent. In all cases where the separation proved satisfactory, the experiments were repeated after varying the amounts of the other constituents, in order to eliminate possible errors due to special conditions.

Details of the method as finally adopted, are given below. The solution should have a volume of about 400 c.c., and sufficient HCl must be present to prevent the precipitation of magnesia on the addition of ammonia. The liquid is heated to boiling, and ammonia added in the usual way in slight excess. Bromine water is then run in by means of a tap funnel, the stem of which is drawn out to a fine jet, and small additional quantities of ammonia are simultaneously added, in order to keep the solution alkaline.[2]   When all the bromine has been added, a few more drops of ammonia are added, the solution boiled, and the precipitate filtered off. It is redissolved in dilute HCl containing a little H_2O_2, and the precipitation repeated exactly as before. The quantity of bromine required depends on the amount of manganese present ; suitable amounts are shown below :

> 10 mgms. of MnO require the addition of 15 c.c. saturated Br water.
> 50   „   „   ,,   ,,   40   „   „
> 100 „   „   ,,   ,,   75   „   „

The results of two typical series of experiments carried out to determine the validity of the above method of precipitation are given in the

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[1] After concentration of the solution and removal of the small amount of alumina still present (vide W. F. Hillebrand, The analysis of silicate and carbonate rocks. Bull. U.S. Geol. Survey, 1919, no. 700, p. 114).

[2] Free acid is produced in the reaction, and it is essential to add sufficient ammonia to ensure the liquid remaining alkaline throughout the precipitation.

annexed tables. In all cases a double precipitation with ammonia and bromine was made. The solution used contained, in addition to the quantities of lime and magnesia shown in the tables, Al_2O_3 0·175 and Fe_2O_3 0·1 gram as the chlorides of these metals. It will be seen that the separation of the manganese is quite satisfactory up to a limit of about 50 milligrams MnO ; above this they are liable to be irregular, some co-precipitation of lime and magnesia resulting. The above limit is, however, ample as regards the quantities of manganese met with in the analysis of igneous rocks, which is the particular case that the method is devised to cover.

In order to ascertain that the whole of the manganese introduced into the solution was recoverable from the ammonia precipitates, those obtained in the second series of experiments were dissolved in HCl, taken down to strong fuming with sulphuric acid, and the manganese in the resulting solution determined by the bismuthate method. The following results were obtained :

MnO originally present in solution.	MnO found in the ammonia precipitate.
0·0049 gram	0·0044 gram
0·0098	0·0095
0·0197	0·0197
0·0492	0·0488

Series I.

No. of Experiment.		Amount MnO (added).		Amount CaO (found).		Amount $Mg_2P_2O_7$ (found).
Check A	...	none	...	0·0637 gr.	...	0·1425 gr.
Check B	...	none	...	0·0634	...	0·1437
Check C	...	none	...	—	...	0·1425
1.	...	0·0010 gr.	...	0·0639	...	0·1420
2.	...	0·0025	...	0·0632	...	0·1438
3.	...	0·0053	...	0·0635	...	0·1421
4.	...	0·0053	...	0·0630	...	0·1428
5.	...	0·0101	...	0·0639	...	0·1432
6.	...	0·0101	...	0·0638	...	det. spoilt
7.	...	0·0201	...	0·0632	...	0·1428
8.	...	0·0201	...	0·0634	...	0·1422
9.	...	0·0503	...	0·0635	...	0·1414
10.	...	0·0503	...	0·0638	...	0·1424

Series II.

No. of Experiment.		Amount MnO (added).		Amount CaO (found).		Amount $Mg_2P_2O_7$ (found).
Check A	...	none	...	0·2102 gr.	...	0·1754 gr.
Check B	...	none	...	0·2108	...	0·1757
1.	...	0·0049 gr.	...	0·2099	...	0·1768
2.	...	0·0098	...	0·2108	...	0·1754
3.	...	0·0197	...	0·2113	...	0·1759
4.	...	0·0492	...	0·2105	...	0·1751
5.	...	0·0492	...	0·2102	...	0·1753
6.	...	0·0738	...	0·2012	...	0·1767
7.	..	0·0738	...	0·2104	...	0·1539
8.	...	0·0738	...	0·2100	...	0·1669
9.	...	0·0984	...	0·2010	...	0·1762
10.	...	0·0984	...	0·2086	...	0·1722
11.	...	0·0984	...	0·2071	...	0·1705
12.	...	0·0984	...	0·2079	...	0·1746
13.	...	0·0984	...	0·2096	...	—
14.	...	0·0984	...	0·2097	...	—