

*The determination of small amounts of copper in rocks.*

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[Read June 7, 1934.]

IN modern petrology increasing importance is being attached to the content of minor chemical constituents, the determination of which is now frequently required, whereas hitherto they have usually been disregarded. In consequence, methods for their accurate determination in small amount have not always been fully worked out. Copper is a case in point, and it is already clear that the method here advocated will show that this metal is much more widely distributed in rocks than is generally realized. Moreover, the use of a large sample, such as 20-50 grams, is no longer necessary.

In attempting to apply to rocks the very sensitive colorimetric method described by T. Callan and J. A. Russell Henderson,<sup>1</sup> various difficulties were encountered, and modifications were developed whereby the method can be adapted to the determination of from 0.001-0.25 % of CuO in silicate rocks and minerals. The reagent used is sodium diethyl-dithio-carbamate, which gives a yellow colour with copper in slightly ammoniacal solution. The authors give a list of other metals which also give a coloration or turbidity with this reagent. The following, taken from their list, are the metals which are present in rocks and the reactions they give :

Copper	...	...	yellow
Aluminium	...	...	white
Ferrous iron	...	...	brown
Ferric iron	...	...	deep brown
Manganese	...	...	very faint turbidity
Nickel	...	...	yellow white turbidity
Titanium	...	...	yellowish-white turbidity
Zinc	...	...	white turbidity
Chromium	...	...	very faint turbidity

<sup>1</sup> T. Callan and J. A. R. Henderson, *Analyst*, London, 1929, vol. 54, p. 650.

In addition to the above list, N. Strafford<sup>1</sup> states that bismuth also gives the same colour as copper. However, Hillebrand and Lundell<sup>2</sup> state 'It is quite safe to say that bismuth will not be encountered in the analysis of rocks and rarely in that of minerals'. In any case, it is precipitated by ammonia. The writer finds that thallos salts cause a serious turbidity, and it is necessary for minerals separated in Clerici solution to be washed very thoroughly with hot water before examination. Chromium, zinc, nickel, and manganese are incompletely precipitated by ammonia, but the amounts of the first three of these in rocks are insufficient to have a disturbing influence. In the case of the sixteen copper determinations given in the table (p. 39) it was found that, after precipitation by ammonia, no turbidity resulted in any one case, although the MnO originally present varied from 0.08 to 0.38%. Experiments conducted with a standard titania solution showed that 0.002 gm. of TiO<sub>2</sub>, in 10 c.c. of the reagent and 90 c.c. of water made slightly ammoniacal, was sufficient to give a yellow brown colour, together with an appreciable turbidity. Fortunately titania is completely precipitated by ammonia. The organic reagent, however, is extremely sensitive to iron. It is therefore evident that the separation of the undesirable constituents by precipitation with ammonia has to be performed with the greatest care.

The most convenient method of decomposing the rock to ensure the inclusion of any copper present as silicate is clearly attack by a mixture of sulphuric and hydrofluoric acids.<sup>3</sup> It was found, however, that in spite of the utmost care in the ammonia precipitation, the filtrate usually gave a strong iron reaction with the reagent. Indeed an ammoniacal filtrate, free from the turbidity and coloration due to colloidal ferric hydroxide, may sometimes contain sufficient iron to render a colorimetric comparison for copper grossly inaccurate, if not impossible.

It appeared that either SO<sub>4</sub> ions, or fluorine in complex ions of the type [FeF<sub>6</sub>], were causing incomplete precipitation of the iron. This

<sup>1</sup> N. Strafford, The detection and determination of small amounts of inorganic substances by colorimetric methods. London (Institute of Chemistry), 1933.

<sup>2</sup> W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analysis. New York and London, 1929, p. 186.

<sup>3</sup> If preferred, the decomposition may be effected by fusion, followed by a separation of silica, and then by the ammonia precipitations. It requires slightly more time in manipulations than the procedure here described. Moreover, the large amount of sodium chloride present causes some turbidity with the organic reagent.

was partially confirmed by the discovery that, after very thorough evaporation to dryness, followed by an hour or more of baking, the precipitation of the iron was complete. The following series of experiments showed that both the  $\text{SO}_4$  ion and the complex fluorine ions were causing the trouble. 4 grams of iron alum were dissolved in 50 c.c. of concentrated hydrochloric acid and made up to a litre. 100 c.c. of the solution were taken for each of the experiments 1-3, diluted to 200 c.c., and the ammonia precipitation carried out with the following modifications and results :

1. 1 c.c. of sulphuric acid was added. The filtrate gave a pronounced brown colour on the addition of only four or five drops of a 0.1 % solution of the reagent. The precipitate was dissolved in hydrochloric acid and re-precipitated. The reaction of the second filtrate with the reagent was nearly as marked as the first. A further precipitation, however, effected a complete separation. After standing for several days the first two filtrates precipitated their iron as the hydroxide.

2. 0.5 gram of sodium fluoride was added. The filtrate gave a reaction with the reagent which was practically the same as in experiment 1. On re-precipitation the colour reaction of the filtrate was undiminished.

3. The experiment was repeated with iron-alum alone. The iron reaction of the filtrate was just the same as in experiment 1. The iron in the filtrate obtained on re-precipitation, however, appeared to have been reduced to about one-third of that from the first precipitation.

4. An ammonia precipitation was carried out on a solution of ferric chloride (1 gm. in 200 c.c. of water and 5 c.c. of concentrated hydrochloric acid). The filtrate gave no coloration with the reagent.

It is concluded from these experiments that free sulphuric acid, large concentrations of sulphates, and the presence of fluorine, all give rise to incomplete precipitation of iron. Fluorine can be completely removed by two evaporations of the acid mixture to strong fuming, followed by evaporation to dryness. Baking for several hours at about  $300^\circ\text{C}$ . removes free sulphuric acid and, on subsequent solution in hydrochloric acid, the sulphate ion concentration is apparently insufficient to interfere with the precipitation of iron if two or more precipitations are made. In practice, only the first filtrate was found occasionally to contain traces of iron, but this can be removed by the cautious addition of dilute barium chloride followed by some more

ammonia, further boiling, and filtration through a double 40 Whatman paper. Excess of barium chloride should be avoided as it gives a slight turbidity with the reagent. It is necessary only to reduce the sulphate ion concentration. If the baking is thoroughly carried out this treatment will not be necessary. It would appear that sulphates, when in sufficient concentration, cause a little iron to run through the filter paper in the colloidal state, but the presence of fluorine is much more serious since it allows iron to pass through in solution.

Callan and Russell Henderson state that if iron and alumina are present they may be removed by adding excess of ammonia and determining copper in the filtrate. Nevertheless, it is generally recognized that copper is incompletely separated in this way.<sup>1</sup> To ascertain both the extent to which copper is retained in the ammonia precipitate and the applicability of this colorimetric method to rock analysis, the following experiments were conducted on sixteen analysed specimens from the Malvern Hills. This was a varied collection of plutonic, hypabyssal, and metamorphic rocks ranging from 45 to 70 % of silica, as well as ferromagnesian minerals separated from them, in all of which not less than twenty-two constituents had been determined.

*The method* used and recommended for the determination of small quantities of copper in silicate analysis is as follows. Two grams of rock powder are heated in a platinum dish on a sandbath with 15 c.c. of 1:1 sulphuric acid and 30 c.c. of hydrofluoric acid until the mixture fumes strongly. After cooling, water is added and the mixture is again evaporated to strong fuming. The temperature is then raised to fume off the sulphuric acid. This is carried on to dryness and the residue baked for several hours at about 300°C. The residue should be broken down and stirred from time to time to assist in the expulsion of sulphuric acid. The dried cake is treated with about 15 c.c. of fairly concentrated hydrochloric acid on the water-bath and, after ten minutes, is diluted to about 50 c.c. and further heated until almost complete solution results. The liquid is filtered, and after the addition of a further 10 to 20 c.c. of concentrated hydrochloric acid, the ammonia precipitation is carried out under the standard conditions (see Hillebrand and Lundell), but with the addition of several c.c. of 1:1 ammonia in excess. The liquid is then boiled for three to five minutes, filtered through a double 41

<sup>1</sup> W. F. Hillebrand and G. E. F. Lundell, *loc. cit.*, p. 70. L. A. Haddock and N. Evers, *Analyst*, London, 1932, vol. 57, p. 495.

Whatman filter paper, and washed three times with boiling  $2\frac{1}{2}$ % ammonium chloride solution containing a few drops of ammonia (the use of an indicator in the wash liquid is inadmissible). The precipitate is removed from the paper, dissolved in 5 c.c. of concentrated hydrochloric acid, re-precipitated, and filtered as before with a double filter paper. Each filtrate is made up to 250 or 500 c.c.,<sup>1</sup> an aliquot part taken, and the colorimetric comparison carried out exactly as described by Callan and Russell Henderson, using a standard copper solution<sup>2</sup> containing 0.00001 gm. Cu per c.c. If more than 0.0001 gm. Cu is present in 100 c.c. turbidity is developed with the reagent and further dilution is required. The presence of the merest trace

Table showing retention of copper by the ammonia precipitate.

Spec. no.	Amount taken	CuO in filtrates from			% retention in 1st ppt.	Total iron as Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> %	Total R <sub>2</sub> O <sub>3</sub> ppt. %
		1st pptn. %	2nd pptn. %	3rd pptn. %				
1	2.0258	0.011	0.0016	—	14.5	8.27	17.75	27.81
2	2.1704	0.014	0.0043	—	30.7	12.87	15.28	30.02
3	1.3293	0.046	0.0041	—	8.9	9.67	15.36	26.20
4	1.0454	0.034	0.0068	—	20.0	13.39	15.02	30.93
5	2.0656	0.016	0.0074	—	46.2	14.81	15.07	32.48
6	2.0734	0.023	0.012	0.006	52.2	9.80	15.69	26.69
7	2.0448	0.031	0.0043	—	14.0	13.16	14.75	30.16
8	2.4782	0.073	0.0098	0.007	13.4	8.43	10.42	19.54
9	1.7975	0.012	0.0076	0.0056	63.3	11.19	8.60	22.14
10	2.4103	0.005	0.0033	0.0017	71.7	11.44	20.40	33.88
11	2.2370	0.008	0.0014	—	17.5	2.79	14.52	17.72
12	2.0992	0.022	0.0052	—	23.6	11.36	16.68	29.71
13	1.1959	0.018	0.0099	—	55.5	12.28	16.16	29.74
14	0.9824	0.030	0.019	0.009	60.3	18.51	10.32	31.86
15	0.4991	0.065	0.023	0.007	35.4	14.97	15.77	31.42
16	0.6747	0.063	0.010	—	15.9	6.57	15.70	22.43

*Nature of Specimens.*—1 and 2. Greenstone. 3. Basic xenolith. 4. Hybrid. 5. Greenstone. 6. Basic xenolith. 7. Greenstone. 8. Biotite-pyroxenite. 9. Hornblendite (almost pure hornblende). 10. Epidosite. 11. Granite. 12. Hybrid sill. 13. Hybrid. 14. Hornblende separated from no. 13. 15. Biotite separated from no. 8. 16. Phlogopite separated from no. 8.

*Note.*—In the case of specimens 9 and 10, the determinations were made by the Rev. A. F. Smethurst, B.Sc., A.R.C.S., F.G.S. The others were carried out by the writer.

<sup>1</sup> In the majority of cases 250 c.c. is the most suitable volume.

<sup>2</sup> It has been found that this solution hydrolyses on keeping. It is best to prepare it freshly by dilution from a solution containing 0.0001 gm. Cu. This is prepared from A. R. copper sulphate and should contain a few drops of sulphuric acid.

of iron in the test solution gives a brown tint with the organic reagent which is readily detected on comparison with the other tube containing copper as the only metal. The addition of some gelatin solution, as recommended by Strafford (*loc. cit.*), increases the brilliance of colour somewhat, thereby facilitating comparison.

The figures given in the table show that an appreciable amount of copper is retained by the ammonia precipitate. The average retention in these sixteen cases is 33.9 %, though in several it is as low as 10–15 %. Nevertheless, a second precipitation is always necessary, and the copper content of the filtrate from this will show whether a third precipitation is required. If the copper content is above 0.05 % a third precipitation is necessary, and in some cases with less than this amount. The use of a considerable excess of ammonia appears to have no effect on the degree of retention, and the alumina thereby re-dissolved is found to be insufficient to have any effect on the colorimetric comparison. Moreover, it has the advantage of precipitating the iron more completely, and in a form less liable to run through the filters.

When the percentage retention is plotted against the  $R_2O_3$  content, the retention curve, though irregular, rises with extreme rapidity after the  $R_2O_3$  exceeds about 25 %. It is evident, therefore, that with very basic rocks several re-precipitations will be necessary. There appears to be no direct relation between the retention and proportions of iron and alumina, but only to the total  $R_2O_3$  content.

*Correction for CuO in  $R_2O_3$  precipitate.*—Unless the retention of copper is shown to be high even after the re-precipitation of the ammonia precipitate, a correction for copper in the  $R_2O_3$  precipitate of the main portion (which has also been precipitated twice) will usually not be necessary. If the degree of retention shows such a correction to be desirable for very accurate work, an approximation to this correction is obtained by determination of copper in the filtrate from the third precipitation.

*Indication of presence of appreciable copper.*—When it is dry, the residue from the first evaporation of a rock powder with a mixture of hydrofluoric and nitric acids (as in the determination of  $P_2O_5$ ) sometimes shows a greenish tinge, which appears to be decidedly more marked when the copper content is appreciable. This colour is never visible after the second and third evaporations, for it is then masked by the deep brown of ferric salts.

*Condition in which the copper occurs.*—Though specimens of sulphide

ores of copper have been found there, the Malvern Hills can scarcely be said to have been mineralized. Sulphur has been determined in all the specimens mentioned in this paper. It does not always vary directly as the copper content, but in the majority of cases there is sufficient sulphur to make chalcosine. In two or three cases no sulphur or only a trace was recorded. As much as 0.04 % of metallic copper only requires 0.01 % of sulphur to form chalcosine or 0.02 % for chalcopyrite. In view of these circumstances and the fact that the method for the determination of copper is much more accurate than those for sulphur, it is inadvisable to conclude that the presence of copper in the absence of sulphur indicates the location of the metal in a silicate mineral unless the excess of copper over requisite sulphur is considerable—say 0.1 %.

*Safeguards against contamination by copper.*—The use of brass sieves in the crushing of the sample should be avoided. Contamination through prolonged heating on a copper water-bath is reduced to a minimum, since only twenty minutes of such heating is required. Nevertheless, it is best to have the bath boiling only gently so that spurting from the sides with possible introduction of copper cannot take place. The reagents used, including the distilled water, should be tested for copper.

*Acknowledgements.*—I wish to acknowledge my indebtedness to Assistant Prof. H. F. Harwood, who first brought the use of this reagent to my notice, and suggested that it might be applied to rock analysis. Assistant Prof. A. Brammall very kindly gave his consent to the incorporation of data obtained in the course of analysis of his specimens. My thanks are also due to Professors P. G. H. Boswell and J. C. Philip for the facilities afforded me in the Geochemistry Laboratory of the Imperial College of Science and Technology.

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