The determination of ferrous iron in resistant silicates.

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THE determination of ferrous iron in minerals, such as staurolite and kornerupine, which cannot be effectively dissolved by dilute sulphuric and hydrofluoric acids has been made possible on the macro-scale by the work of H. P. Rowledge;[1] the mineral is fused with sodium fluoride and boric oxide at 900° C. in a sealed pyrex glass tube, the fusion cake dissolved in hot dilute sulphuric acid in a current of carbon dioxide, and the solution titrated with potassium permanganate. We have met with no difficulty in applying the method on the macro-scale, but when only small amounts of a mineral are available several difficulties arise, and modifications become necessary.

The air present in the sealed tube of a Rowledge fusion, using the quantities and dimensions he specifies, is already sufficient to oxidize about 3 to 5 mg. of ferrous oxide. But when the weight of the sample is reduced to 10 mg., it is not possible to reduce the dead-space in the tube in proportion; it can hardly be reduced below about ¼ c.c. which is sufficient to oxidize 0·3 mg. or 3% FeO and is likely to be more effective in this direction than on the larger scale, since the surface of the fusion is proportionally greater. It is therefore necessary to perform the fusion either in vacuo or with the tube filled with an inert gas. Vacuum fusion is more convenient, and though it was anticipated that the rather thin-walled evacuated tubes would collapse at 900° C., this fear proved unfounded; indeed, if the fused mixture of sodium fluoride and boric oxide was not freshly dried, enough moisture was occasionally present to cause dangerous bulging; thicker-walled tubing than could be handled with the blowpipe at our disposal would be preferable.

A far more serious difficulty was that of dissolving the fusion without oxidation of the ferrous iron; solution in hot dilute sulphuric acid with or without an addition of boric acid was very slow, and it was found very difficult to exclude every trace of air. This might be met by adding a

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[1] H. P. Rowledge, Journ. Roy. Soc. Western Australia, 1934, vol. 20 (for 1933–1934), p. 165. [M.A. 6–191.]

known amount of oxidizing agent to the solvent and back-titrating the excess. The oxidizing agent would have to be perfectly stable in hot dilute solution (about 0·01 N or less) for two hours or more, even in presence of hydrofluoric or hydrofluoric and boric acids; potassium permanganate is quite unsuitable, and L. A. Sarver[1] has shown that potassium dichromate is not sufficiently stable in presence of hydrofluoric acid; we have found that an addition of boric acid does not remove this disability. Ceric sulphate seemed very promising; 0·1 N solutions showed no appreciable loss when boiled for 30 minutes with dilute hydrofluoric and sulphuric acids, and the reagent may well be found serviceable for macro-determinations of ferrous iron in non-resistant minerals,[2] but the stability of more dilute solutions is inadequate.

The problem was solved by the use of 0·005 M iodine monochloride in strong hydrochloric acid as an oxidizing solvent; this reagent dissolves the coarsely crushed fusion in about an hour in the cold, and oxidizes the ferrous iron with liberation of iodine: $2Fe^{\cdot\cdot}+2ICl+2H^{\cdot} = 2Fe^{\cdot\cdot\cdot}+2HCl+I_2$. The iodine is re-oxidized with standard potassium iodate to iodine monochloride (which thus plays a purely intermediary part, serving only to prevent air oxidation of ferrous iron) using carbon tetrachloride as indicator. The titration is a very favourable one, as the end point can easily be observed with an accuracy of 0·02 c.c. of 0·0005 M (molar) iodate, equivalent to 0·003 mg. FeO, even in presence of powdered glass (which tends to keep the carbon tetrachloride dispersed).

This method for the solution and titration of the fusion cake is also very convenient and advantageous for a Rowledge fusion on the macro-scale, avoiding any danger of air oxidation, and could be applied directly to olivine and other minerals soluble in cold strong hydrochloric or hydrochloric and hydrofluoric acids.

The modified procedure as adapted for the micro-scale is as follows: a tube of pyrex glass, of 3 mm. bore and as thick-walled as can be worked with the means available, is closed at one end and drawn out into a filling funnel about 3–4 cm. from the closed end; into this tube are weighed 10 mg. of the mineral and 100–150 mg. of Rowledge's flux (2 parts $NaF+1$ part B_2O_3, freshly fused and powdered; if it gets damp the tube may be bulged or even burst); the tube is evacuated with a good water pump ($<$ 16 mm. Hg) and sealed under vacuum, the mineral and flux mixed by rotation and shaking, and the tube bedded upright in sand in a tall crucible; after fusion for $\frac{1}{2}$–$\frac{3}{4}$ hour at 900° C. in a muffle or

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[1] L. A. Sarver, Journ Amer. Chem. Soc., 1927, vol. 49, p. 1472.

[2] Experiments have been commenced in this connexion.

electric crucible furnace the tube is removed, and laid in a mortar to cool; it is broken with the pestle and as much of the glass as can be freed from the cake removed, the rest being coarsely powdered with the cake. The powdered cake is transferred to a 25 or 50 c.c. flask, preferably glass-stoppered, though a new cork will serve, and dissolved in 5 c.c. or more of a roughly 0·005 M solution of iodine monochloride in 1 : 1 hydrochloric acid[1] and an equal volume of strong hydrochloric acid, rinsing the mortar with the acid (1 c.c. of iodine monochloride will be required for each 1 % of FeO expected, together with a small excess); after about one hour with occasional shaking the cake should be dissolved; from ½ to 1 c.c. of carbon tetrachloride is added and the solution titrated with 0·0005 M potassium iodate ($4Fe^{\cdot\cdot}+IO_3'+6H^{\cdot}+Cl' = 4Fe^{\cdot\cdot\cdot}+3H_2O+ICl$). The titrated solution should not develop any free iodine on standing an hour in the stoppered flask; if it does, the solution of the cake was probably incomplete, and the newly liberated iodine should be titrated; the re-titrated solution is set aside again to make sure that solution is complete.

Using this procedure, 2·30 % FeO was found in a rock which gave 2·15 % by the Pratt method.[2] The rock also contained a trace of sulphide; if this were pyrite, it would not be attacked in the Pratt method, but its sulphur content would reduce ferric iron in the Rowledge method, and would appear as 17 times its weight of FeO. In five kornerupine analyses (this vol. p. 124), duplicate FeO determinations were in good agreement.

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[1] 0·18 g. KIO_3 and 0·28 g. KI in 250 c.c. conc. HCl and 250 c.c. water; add a little CCl_4, and if free iodine is present, add very dilute KIO_3 drop by drop till it is removed; if absent, add a few drops of dilute KI till it appears and then remove with KIO_3; store in the dark; if iodine develops on standing, remove with KIO_3.

[2] J. H. Pratt, Amer. Journ. Sci., 1894, ser. 3, vol. 48, p. 149.