A Method for the Direct Titrimetric Determination of Iron(III) in Silicate Rocks

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The rock sample is decomposed with hydrofluoric acid in the manner of a conventional iron(II) determination, and the iron(III) in the resulting solution is determined by titration with a solution of ferrocene (dicyclopentadienyliron) in 2-methoxyethanol. A modified procedure is necessary for rocks of very high magnesium content, and it is indicated that errors may arise in the conventional iron(II) determination when applied to rocks of this type.

THE iron(III) content of silicate rocks is normally calculated by difference from the results obtained for total iron and iron(II), and the results of collaborative studies of rock analysis show that, among the major constituents, the result for iron(III) is one of the least reliable, mainly on account of uncertainties in the iron(II) determination. For the total iron determination various well known methods are available, while the iron(II) is commonly determined by some variant of the Pratt method.[1] In this method, the sample is first decomposed by heating in a covered platinum crucible with a mixture of dilute hydrofluoric and sulphuric acids. The contents of the crucible are then quickly added to an excess of boric acid solution and the iron(II) is titrated with a standard solution of an oxidant such as dichromate. In the absence of a convenient and generally accepted method, the direct determination of iron(III) in the solution thus prepared is not normally attempted but this could, in principle, provide a more accurate value for iron(III) than that derived by difference, especially when the ratio of iron(III) to iron(II) is low.

The titrimetric determination of iron(III) in solution by titration with ferrocene (dicyclopentadienyliron) has been proposed by Wolf, Franz and Hennig[2] and is based on the reaction

$$Fe(C_5H_5)_2 + Fe^{3+} \rightarrow Fe^{2+} + Fe(C_5H_5)_2^{+}$$

In the presence of thiocyanate ions the end-point is indicated by the disappearance of the red colour of iron(III) thiocyanate and its replacement by the blue colour of the ferricenium ion.

As there is a high degree of specificity for iron(III) and the reaction takes place in dilute mineral acid solution, there appeared to be a possible application to iron(III) determination in solutions prepared as for the conventional iron(II) procedure. The stoicheiometry of the titration was first examined and the reaction was found, under these conditions, to be quantitative. However, the presence of a suitable wetting agent appeared to be essential; the wetting agent presumably acts by ensuring the effective dispersion of the ferrocene in a finely divided and reactive form. A number of preparations were tried in this connection but some of them caused interference by interaction with the iron(III) thiocyanate complex or by causing cloudiness in the solution. The wetting agent finally selected (see under Reagents) is satisfactory in both of these respects and is of the non-ionogenic type with a poly(ethylene glycol) chain.

EXPERIMENTAL

REAGENTS—

All reagents should be of analytical-reagent grade when available.

Sulphuric acid, 50 *per cent.* V/V—Add 1 volume of concentrated sulphuric acid (sp. gr.

1·84) cautiously, with stirring, to 1 volume of water and finally dilute the mixture, when cool, back to 2 volumes.

Hydrofluoric acid, 40 *per cent*. m/m.

Boric acid solution, saturated.

Boric acid.

Ammonium thiocyanate solution, 5 *per cent*. m/V.

Lissapol NDB solution—A 5 per cent. *V/V* solution of Lissapol NDB detergent liquid (distributed by Hopkin & Williams Ltd., by arrangement with Imperial Chemical Industries Ltd.) in 95 per cent. *V/V* ethanol.

Ferrocene solution—Dissolve 0·5830 g of ferrocene (dicyclopentadienyliron) in 2-methoxy-ethanol and dilute the solution to 500 ml with the same solvent. This solution is stable if stored in a glass-stoppered bottle.

Potassium permanganate solution, 0·1 *per cent*. m/V.

Standard iron(III) solution—Dissolve 0·4911 g of ammonium iron(II) sulphate in about 25 ml of water containing 10 ml of the sulphuric acid (50 per cent. *V/V*) and add a small excess of bromine water. Evaporate the solution until fumes of sulphuric acid appear, then cool it and cautiously add about 100 ml of water. Heat the mixture until a clear solution is obtained, then transfer it to a 500-ml calibrated flask, cool to room temperature and dilute the solution to the mark: 1 ml of this solution contains the equivalent of 0·2 mg of iron(III) oxide. Prepare an iron(III) spike solution by diluting one volume of standard iron(III) solution with four volumes of water.

In order to check the iron content of the ammonium iron(II) sulphate, dissolve 1 g in water, oxidise the solution with bromine water and precipitate the iron as iron(III) hydroxide with ammonia from the hot solution. Filter off the precipitate, ignite it at 1000 °C and weigh the resulting iron(III) oxide (Fe_2O_3).

Procedure—

To a clear, plastic 250-ml beaker add 100 ml of saturated boric acid solution and to a similar 100-ml beaker add 50 ml of the same solution. Set these items aside.

To 0·5000 g of rock sample powder (ground to pass a 100-mesh sieve) in a platinum crucible of 60 to 80-ml capacity with a close-fitting lid, add a few millilitres of water and 10 ml of 50 per cent. *V/V* sulphuric acid. Add more water approximately to half-fill the crucible and heat to boiling over a small flame protected from draughts. After a few seconds' boiling add 10 ml of hydrofluoric acid without interrupting the heating, replace the lid immediately and note the time at which boiling recommences. After 10 minutes' boiling remove the flame and quickly rinse condensate from the lid into the crucible with boric acid solution from the 100-ml beaker. Then add further boric acid solution so as almost to fill the crucible and, with the aid of tongs, tip the contents of the crucible without delay into the 100 ml of boric acid solution in the prepared 250-ml beaker. Rinse any material left in the crucible into the beaker with the remainder of the boric acid solution in the 100-ml beaker and then transfer the whole contents into a 200-ml calibrated flask, rinsing with boiled, air-free water. Cool the flask to room temperature under running water and dilute to the mark with air-free water.

Transfer a 20-ml aliquot of the solution into a 150-ml glass beaker and dilute it with water to about 75 ml. Stir the solution with a magnetic stirrer and, after adding 10 ml of ammonium thiocyanate solution and 2 ml of Lissapol NDB solution, titrate it against ferrocene solution from a burette graduated in 0·05-ml divisions. The end-point is indicated, in good white light, by the appearance of a blue colour without any trace of red iron(III) thiocyanate colour. Add 1 ml of the iron(III) spike solution and again titrate to the same end-point, this time noting the total volume of titrant (*X* ml) added. Carry out the above titration procedure on 1 ml of iron(III) spike solution to which has been added 1 ml of dilute sulphuric acid before dilution to 75 ml, and note the volume of titrant (*s* ml) required.

In order to standardise the ferrocene solution transfer 10 ml of standard iron(III) solution into a 150-ml beaker by means of a pipette and add permanganate solution dropwise until there is a small visible excess, then dilute the mixture to 75 ml and proceed as above, including the addition of 1 ml of iron(III) spike solution. Note the total volume of titrant (*S* ml) required.

CALCULATION—

Iron(III) oxide in sample, per cent. $= \dfrac{4\,(X-s)}{S-s}$

RESULTS AND DISCUSSION

With the exception of PCC-1 and DTS-1, the rocks listed in Table I were analysed by the procedure given above. This standard procedure gave very low results (0·21 and 0·04 per cent. for PCC-1 and DTS-1, respectively) when applied to these very magnesium-rich rocks. Cloudy solutions were invariably obtained, but this did not seriously obscure the end-point of the titration and it was suspected that the white insoluble material, although essentially magnesium fluoride, might contain coprecipitated iron(III) fluoride. This white solid could be brought into solution by adding a further 3 g of solid boric acid to the solution in the 200-ml flask and heating on the water-bath for about 45 minutes. After cooling and diluting to the mark, 20-ml aliquots were taken for titration in the usual way and a marked increase in the iron(III) value was found (Table I). As this result could have been caused, at least in part, by atmospheric oxidation of iron(II) in the solution, determinations were carried out on 100-ml aliquots of the same solution of iron(II) by titration with dichromate solution.

TABLE I
RESULTS OBTAINED ON SOME STANDARD ROCKS BY USING
THE PROPOSED METHOD

Rock	Iron(III) oxide, per cent.			
	Operator 1	Operator 2	Operator 3	Other methods
Granite G-1	0·86	0·84	0·86	0·87*
Diabase (dolerite) W-1	1·32	1·47	1·38	1·40*
Granite G-2	1·08	1·06	1·06	1·01†
Granodiorite GSP-1 ..	1·63	1·63	1·67	1·60†
Andesite AGV-1	4·39	4·42	4·43	4·39†
Peridotite PCC-1 ..	2·06‡	2·06‡	2·06‡	2·49†
Dunite DTS-1	0·38‡	0·41‡	0·37‡	0·85†
Basalt BCR-1	3·36	3·45	3·47	3·45†

* Flanagan.[3]
† Abbey.[4]
‡ Variant of method, used for magnesium-rich rocks (see text).

The results of these determinations for PCC-1 and DTS-1 (5·39 and 7·21 per cent. of iron(II) oxide, respectively) do not support this atmospheric oxidation explanation. The results can be compared with those (5·24 and 7·23) in the most recent report by Flanagan[3] on values for international reference samples and are considerably higher than those appearing in the earlier Flanagan report[5] (4·94 and 6·79) and also higher than the figures proposed by Abbey[4] (5·14 and 6·98) after a critical study of this earlier report. The tendency to obtain maximum values for both iron(III) and iron(II) after dissolving the magnesium fluoride precipitate indicates that both forms of iron are, to some extent, segregated in the precipitate. So far as the present authors are aware this is a possible source of error in the conventional iron(II) determination that has not previously been reported and which should be borne in mind when rocks of very high magnesium content are being analysed.

The blue colour of the ferricenium ion, when sufficiently intense, tends to obscure the end-point of the titration, which, for this reason, is most successful with relatively dilute solutions of iron(III). In practice, under the conditions prescribed for the procedure, the most satisfactory working range of the method is up to about 5 per cent. of iron(III) oxide in the sample. This, however, is not a serious limitation as most silicate rocks fall within this range.

The proposed method will not avoid certain errors that affect the accuracy of the conventional iron(II) determination. These errors are discussed in some detail by Maxwell[6] and commonly include those due to the presence of carbonaceous matter and sulphides in the sample. However, the mineral pyrite, which is the most frequently encountered sulphide

in silicate rocks, is not normally attacked by the acid mixture used in this method and so will not affect the iron(III) titration. It would, if not allowed for, be recorded as iron(III) if that value was calculated by difference from the total iron and iron(II) results. The use of a spiking procedure in the titration serves to correct for any iron(III) in the titration reagents. It also allows the first tentative end-point to be over-run and the final definitive end-point to be judged with greater precision.

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