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THE RELATIVE VALUES OF THE MITSCHERLICH AND HYDROFLUORIC ACID METHODS FOR THE DETERMINATION OF FERROUS IRON.[1]

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AMONG determinations in mineral and rock analysis, upon the accuracy of which great stress is laid, is that of iron in the ferrous condition. It is of special importance because an error attaching to it affects in like degree but opposite direction the ferric iron that is also nearly always present. Up to about the year 1867, the only method for its determination giving at all satisfactory results was that of A. Mitscherlich,[2] depending on the decomposition of the mineral at high temperature by rather strong sulphuric acid (3 parts acid to 1 part water by weight) in a sealed tube from which air has been expelled, and subsequent titration of the ferrous iron by permanganate. When pure hydrofluoric acid became a commercial article, the above method gave place in large measure to one depending on the decomposition of the silicate by a mixture of dilute sulphuric and hydrofluoric acids at atmospheric pressure and a tempera-

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[1] Published by permission of the Director of the United States Geological Survey.

[2] *J. prakt. Chem.*, 81, 116 (1860).

ture not above 100° C., care being taken as before to prevent contact with air.[1]

It became known in the laboratory of the United States Geological Survey fully twelve years ago that the two methods generally give discordant results when applied to the same rocks, the Mitscherlich method in such cases always showing the higher figure for ferrous iron. With low percentages of iron the discrepancies were not very great, but they seemed, in general, to increase as the ferrous oxide rose, until, with a rock showing 10 per cent. ferrous oxide by the hydrofluoric acid method, the Mitscherlich method might give 12 per cent. Experiments with artificial ferrous salts threw no light on the subject, for both methods gave with them the same sharp and concordant results.

Until very recently no cause suggested itself whereby the discordance could be explained. In theory, the Mitscherlich method seemed perfect, and it was concluded that, given entire decomposition of all ferruginous minerals, the determinations made by it were nearer the truth than those by the hydrofluoric acid method. That the reverse is true in most cases, appears as the result of work done in this laboratory in an entirely different connection.

In the first place, it had been found by long experience that nearly all rocks carry small amounts of sulphides—pyrite, pyrrhotite, or both—often visible to the eye, but more often in such small amount as to escape direct observation. One of us (Stokes), in an investigation now in progress on the oxidizing action of ferric salts on sulphur, pyrite, and other sulphides, has found that this action is vastly more rapid and complete than has hitherto been suspected; that not only is the metal of the sulphide oxidized, but the sulphur to sulphuric acid as well.

The application of these observations to rock analysis shows that the presence of 0.01 per cent. of sulphur in any unoxidized form may produce a maximum error of 0.135 per cent. in the ferrous oxide determination and the not infrequent amount of 0.10 per cent. of sulphur will multiply this error by 10. One atom of sulphur (32) requires for its complete conversion into trioxide the oxygen of three molecules of ferric oxide (480), which then becomes six molecules of ferrous oxide (432). The

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[1] J. P. Cooke: *Am. J. Sci.* (2), 44, 347 (1867).

case is still worse with the sulphide, since not only the sulphur, but its accompanying metal must be oxidized. The above percentages of sulphur evolved as hydrogen sulphide and fully oxidized would involve errors in the ferrous oxide determination of 0.18 per cent. and 1.80 per cent., respectively. The error caused by sulphides tends to become greater the more there is present of either or both sulphide or ferric salt. Now the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively rich in pyrite and pyrrhotite ; hence the increased discrepancy between the results by the two methods, as the iron contents of the rock rise, is fully in accord with the above explanation.

The following experiments made by Stokes (somewhat out of their contemplated order in his investigation referred to) bear out the above statements most fully and show that the Mitscherlich method for rocks and all minerals which contain even a trace of free sulphur or sulphides is no longer worthy of a moment's consideration.

Experiment 1.—0.0010 gram pyrite was heated with 25 cc. of a sulphuric solution (1 part acid to 3 parts water by weight) of ferric ammonium sulphate (0.0470 gram of ferric oxide) in a horizontally-lying sealed tube for six hours at 175° to 195° C. All air had been carefully replaced by carbon dioxide. The pyrite had nearly disappeared, and titration with permanganate showed a consumption of oxygen equivalent to 0.0068 gram ferrous oxide. Complete oxidation of the pyrite would have required oxygen equivalent to 0.0090 gram ferrous oxide.

Experiment 2.—This was exactly like the first, except that 0.0013 gram pyrite was used. Permanganate was reduced equivalent to 0.0090 gram ferrous oxide. Had oxidation been complete the figure would have been 0.0117 gram.

It is quite possible that in both of these experiments the oxidation would have been complete had the pyrite been disseminated throughout a greater space in the tube, as is the case when rocks and minerals are treated, because of the presence of a gram or thereabouts of diluting quartz and silicates.

Had precisely similar experiments been made with rock powders carrying 0.10 per cent., and 0.13 per cent., of pyrite with

4.7 per cent. of ferric oxide and no ferrous oxide, the following erroneous results might have appeared:

	I.	II.
Ferrous oxide.........	0.68	0.91
Ferric oxide..........	4.00	3.76

To overcome the possible objection that the foregoing experiments were not conclusive as to the worthlessness of the Mitscherlich method in presence of sulphides because the concentration of the acid was very different from the normal, the following sealed tube experiments were made with acid of the normal strength (3 parts acid to 1 part water by weight) without any ferric salt, the belief being that the stronger acid, under the conditions of the experiment, would itself act as an oxidizer.

Experiment 3.—Pyrite 0.0016 gram. Three hours at 195° C. Solution only partial. Consumption of permanganate equivalent to 0.00117 gram ferrous oxide.

Experiment 4.—Pyrite 0.0032 gram. Twelve hours at 220° C. Solution perfect. Odor of sulphur dioxide apparent on opening tube. Consumption of permanganate equivalent to 0.01742 gram ferrous oxide.

Experiment 5.—Sulphur 0.0021 gram. Three hours at 195° C., and, as the sulphur had not disappeared, further six hours at 250° C. Entire disappearance of the sulphur. Consumption of permanganate equivalent to 0.01320 gram ferrous oxide.

Experiment 6.—Sulphur 0.0039 gram. Twelve hours at 220° C. Entire disappearance of the sulphur and strong odor of sulphur dioxide on the opening tube. Consumption of permanganate equivalent to 0.03619 gram ferrous oxide.

In experiments 4, 5, and 6, where decomposition was complete the consumption of permanganate is considerably less than theory requires, but this is explained by the escape of not a little sulphur dioxide on opening the tube. Had a ferric salt been present the consumption of permanganate would undoubtedly have reached that required by theory.

It might be supposed from the foregoing that a similar error would affect ferrous iron determinations by the hydrofluoric acid method. However, experiment has shown that with the amounts of sulphide usually found in igneous rocks their effect is negligible, though by increasing the amount of sulphide the effect becomes more and more apparent because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand,—a temperature of 150°–200° C., and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulphide that may be formed,—the sulphur of the sulphides becomes nearly, if not quite, fully oxidized to sulphuric acid, at the expense of the ferric oxide in the rock, with the production of an equivalent amount of ferrous oxide in addition to that resulting from the iron of the sulphide itself.

In order to obtain quantitative data regarding the effect of pyrite on the ferrous iron estimation by the hydrofluoric acid method, the following tests were recently made by one of us.

Part of a fine crystal of pyrite was rather finely powdered and boiled out with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, or from superficial oxidation of the powder, since a second boiling with fresh acid afforded a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverized. A quarter of a gram of it, when treated with dilute sulphuric and hydrofluoric acids in a large crucible by the Cooke method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter-paper, required but two drops of a permanganate solution representing only 0.0032 gram ferrous oxide to the cubic centimeter.

That the error obtaining under the conditions prevailing in rock analysis might be ascertained, successive portions of one gram each of a hornblende schist free from sulphur and carrying 10.09 per cent. ferrous oxide as the mean of several determinations and 4 per cent. ferric oxide, were mixed in a 60 cc. platinum crucible with 0.02, 0.025, and 0.10 gram, respectively, of the above purified pyrite powder. This mixture was then treated with hydrofluoric and sulphuric acids as above, the water-bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end-reaction by its reducing effect upon the permanganate, the solution was filtered as above and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70 per cent. ferrous oxide. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous iron estimation by the Cooke method is negligible. At the same time, it is to be borne in mind that with increased content, either of ferric iron or of pyrite, an increased amount of pyrite will be attacked and that the extent of this attack is undoubtedly influenced by the degree of fineness of the pyrite powder.

All users of the method have noticed the rapid disappearance in hydrofluoric solutions, when titrating ferrous iron, of the pink color produced by an excess of permanganate. If much ferrous iron be present, many cubic centimeters of permanganate can be added without causing more than a transitory pink coloration. The solution takes on, however, in ever-increasing intensity, the red-brown color characteristic of manganic salts. It seems that manganous fluoride in acid solution is very susceptible to oxidation by permanganate, for the above-mentioned changes take place when permanganate is added to sulphuric and hydrofluoric acids containing some manganous sulphate.

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ON THE DIGESTION AND ASSIMILATION OF PENTOSES AND FURFUROIDS.

BY C. F. CROSS, E. J. BEVAN, AND J. S. REMINGTON.

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THE furfural-yielding constituents of plant tissues continue to be designated by the majority of observers as pentosans. It is probable, however, that the group of natural products thus constituted are of more varied characteristics.

It must be noted first that we have no specialized form of pentosane comparable with starch and that the substances described as such are products isolated by chemical processes in the laboratory and devoid of the well-marked individuality and properties of the hexose-anhydride. We are not aware of any