The fact that iron can be reduced to the ferrous condition and also titrated in the presence of some organic material greatly increases the usefulness and possibilities of the method.

## Summary

1. The ferrous ion is oxidized quantitatively to the ferric ion by iodine chloride and the iodine liberated can be titrated with a standard solution of potassium iodate after adding enough concentrated hydrochloric acid so that the final solution will contain 50% of hydrochloric acid by volume.

2. The ferrous ion can also be determined by adding an excess of standard potassium iodate to a dilute sulfuric acid solution of ferrous ion, and then adding concentrated hydrochloric acid and titrating with a standard potassium iodide solution.

3. The presence of many organic compounds such as acetic acid, succinic acid, tartaric acid, ethyl alcohol, filter paper or formalin does not affect the titration.

4. The method is of especial interest to chemists who are called upon to make occasional analyses, for iodate solutions require no standardization and do not change in strength on keeping.

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[Contribution from the Chemical Laboratory of the University of Michigan]

# THE DETERMINATION OF FERROUS IRON IN SILICATE ROCKS.

## I

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The exact determination of ferrous iron in rocks has been conceded to be the most difficult and least satisfactory of all usual determinations in rock analyses.[1]

The Cooke method[2] as modified by Pratt,[3] Barnebey[4] and others, is probably the one most commonly used.

This method involves decomposition of the crushed rock sample by boiling with hydrofluoric and sulfuric acids in a capacious platinum crucible, transfer of the solution to a beaker containing boric acid and titration of the resulting mixture with standardized potassium permanganate.[5]

There are three obvious objections to the method: (*a*) the need for a fairly large (and therefore expensive) platinum crucible, (*b*) the impossibil-

[1] (a) Hillebrand, U. S. Geol. Survey, *Bull.*, **700**, p. 207; (b) Washington, "The Chemical Analysis of Rocks," John Wiley and Sons, Inc., New York, 3d ed., **1919**, p. 183.

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

[3] Pratt, *ibid.*, [3] **48**, 149 (1894).

[4] Barnebey, This Journal, **37**, 1481 (1915).

[5] For details see Washington, ref. 1b, pp. 186–191.

ity of seeing when decomposition is complete, and (*c*) the necessity of transferring the readily oxidized ferrous solution to another dish for titration.

It is, perhaps, not commonly known that a mixture of hydrofluoric and sulfuric acids can be boiled in Pyrex glassware for some time without perforating the container. The same is true in the case of quartz ware which is, in fact, slightly less rapidly dissolved than Pyrex.

Comparative tests of the two materials have demonstrated that quartz is more satisfactory for the permanganate titration of ferrous iron in that it does not appreciably absorb light at the violet end of the spectrum. Even in a vessel of fairly thick, translucent quartz, a permanganate end-point is more readily discerned than in glass. Furthermore, a warning of the approaching end-point is given by an apparent change in the solution from green to colorless just before the true end-point is reached.

In view of these properties and the difficulties mentioned above, it was decided to try both glass and quartz vessels as containers for the decomposition and titration of rock samples. Data presented here cover the work with Pyrex flasks.

## Procedure

After many exploratory tests, six new, wide-mouthed, Pyrex, Erlenmeyer flasks of 250 cc. capacity were selected.[6]

The flasks, after cleaning, were weighed, using the heaviest one as a counterpoise. When needed, each flask was filled with carbon dioxide and the sample for analysis introduced. This was immediately followed by 15 cc. of water, 10 cc. of dilute sulfuric acid (1:3) and 5–8 cc. of hydrofluoric acid (40%). The flask was next placed on a hot-plate and the liquid gently boiled under a slow stream of carbon dioxide. When, upon swirling the solution, no undecomposed particles were observed, the flask was removed from the hot-plate and a cold, freshly prepared mixture of water (100 cc.), boric acid (6 g.) and sulfuric acid (5 cc. of 1:1) immediately added. After cooling to approximately 15°, which required not over ten minutes, the solution was titrated with standardized potassium permanganate, the amount used being measured in grams.[7] Finally the flask was cleaned and weighed.[8]

## Results

In order to determine whether anything that had gone into solution during the dissolving process would reduce permanganate, blanks were

Table I

Blank Determinations

| Flask no. | Time. min. | Temp., °C. | Glass diss., g. | $KMnO_4$, g. soln. | $\frac{\text{G. } KMnO_4}{\text{G. glass}}$ |
|---|---|---|---|---|---|
| 2 | 25 | 98 | 1.091 | 2.335 | 2.140 |
| 4 | 20 | 98 | 1.020 | 2.173 | 2.130 |
| | | | | Av. | 2.135 |

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[6] While an effort was made to secure samples from different lots, there is no assurance that this objective was attained.

[7] The volume of solution at the end was about 150 cc. for the majority of samples.

[8] The average flask life in this work was found to be about twenty determinations.

run, omitting only the ferrous material. Some of the results are given in Table I, which also includes the duration and approximate temperature of reaction.

A consideration of the analysis of Pyrex glass by Walker and Smither[9] would indicate only two sources of reducing action. Some of the iron or arsenic or both might be in the lower valence rather than the higher, as there reported, since arsenic is commonly added, when making glass, in the form of $As_2O_3$ to reduce any ferric iron present as an impurity in the raw materials. In any case the figures obtained when dividing the weight of glass dissolved by the weight of permanganate consumed apparently cannot be used as a correction factor in an actual analysis (see Table III, col. 5).

The only satisfactory way thus far found to determine the factor is to run a series of determinations using a compound of known ferrous iron content. Under these conditions the excess permanganate consumed, divided by the weight of glass dissolved, does give a dependable factor. This factor can obviously be applied in calculations involving other normalities of permanganate. Data for the correction factor obtained are given in Table II, the standard ferrous ammonium sulfate containing 18.27% of iron as FeO.

TABLE II

DATA USED IN DETERMINATION OF CORRECTION FACTOR

Normality of $KMnO_4$ = 0.04803; $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ = 18.27% FeO; time of boiling = 25 minutes

| Sample, g. | Glass diss., g. | Excess $KMnO_4$, g. soln. | $\frac{\text{G. excess } KMnO_4}{\text{G. glass}}$ |
|---|---|---|---|
| 0.4076 | 1.316 | 1.651 | 1.255 |
| .4079 | 1.395 | 1.739 | 1.247 |
| .4512 | 1.280 | 1.599 | 1.249 |
| | | Av. | 1.250 |

Using the figures 1.250 as a basis for correcting the original data given in Table III, the results in the last column were secured.

TABLE III

ANALYSIS OF MAGNETITE (?) FOR FERROUS IRON. APPLICATION OF CORRECTIONS FOR REDUCTION DUE TO MATERIAL IN GLASS DISSOLVED

Normality of $KMnO_4$ = 0.04972

| Sample g. | Time, min. | Glass dissolved, g. | FeO, % | | |
|---|---|---|---|---|---|
| | | | Uncorr. | C.F.—2.135 | C.F.—1.250[a] |
| 0.3048 | 25 | 1.093 | 41.47 | 38.74 | 39.82 |
| .3035 | 20 | 0.918 | 41.16 | 38.85 | 39.76 |
| .3763 | 20 | .972 | 41.08 | 39.11 | 39.89 |

[a] The correction, considering difference in normality = (0.04972 × 1.250)/0.04803.

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[9] U. S. Bureau of Standards, *Tech. Paper* **107**, p. 8. The figures given are

| $Al_2O_3$ | $Fe_2O_3$ | MnO | CaO | MgO | $Na_2O$ | $K_2O$ | $SiO_2$ | $B_2O_3$ | $As_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|
| 2.0 | 0.25 | 0.01 | 0.29 | 0.06 | 4.4 | 0.20 | 80.5 | 11.8 | 0.70 |

## Notes

1. This material when received was labeled "Magnetite." Obviously the FeO content is almost 9% too high for a true magnetite. It is expected that a complete analysis with mineralogical and geological data will be published elsewhere.

2. Samples for the above analyses were portions of a single crystal, crushed to a coarse powder, about twenty mesh.

In Table IV are given results for a variety of silicate rocks. All samples were crushed to forty mesh and finer.

TABLE IV

ANALYSIS OF SILICATES FOR FERROUS IRON

Normality of $KMnO_4$ = 0.04803

| Sample | Weight, g. | Time, min. | Glass diss., g. | $KMnO_4$ (corr.), g. soln. | FeO, % |
|---|---|---|---|---|---|
| 1 | 0.5376 | 12 | 0.692 | 2.967 | 1.90 |
| | .5340 | 12 | .851 | 2.871 | 1.85 |
| 2 | .3083 | 17 | .912 | 3.843 | 4.30 |
| | .4995 | 19 | 1.463 | 6.291 | 4.35 |
| 3 | .4779 | 8 | 0.374 | 10.981 | 7.93 |
| | .4428 | 8 | .486 | 10.243 | 7.98 |
| | .5433 | 8 | .447 | 12.476 | 7.92 |
| 4 | .4435 | 8 | .419 | 10.805 | 8.41 |
| | .5473 | 7 | .390 | 13.272 | 8.37 |
| | .4872 | 8 | .405 | 11.826 | 8.38 |
| 5 | .5090 | 20 | 1.449 | 15.170 | 10.28 |
| | .5846 | 21 | 0.873 | 17.313 | 10.22 |
| | .6600 | 20 | 1.139 | 19.584 | 10.24 |

No. 1—Andesite, Arakebesan Island; No. 2—Andesite, Bonin Island; No. 3—Basalt, Arizona; No. 4—Basal Basaltic Glass, Arizona; No. 5—Basalt (Ponape), Tolatik Island.

## Summary

1. Platinum ware is not absolutely essential for the determination of ferrous iron in rocks.

2. Silicate samples can be dissolved by boiling with hydrofluoric and sulfuric acids in Pyrex flasks and, subject to the usual interferences, the solution obtained may be titrated for ferrous iron.

3. A glass container has two marked advantages over one of platinum: (*a*) the completeness of decomposition may be readily observed, and (*b*) transfer of the solution from one dish to another for titration is unnecessary.

4. A correction factor for Pyrex glass has been determined.

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