tion of sodium acetate to their hydrofluoric acid solution. It would appear that the Sb^{III} in such a solution, providing a moderate amount of free hydrochloric acid be present, is as completely precipitated by hydrogen sulphide as it is when the solution is first neutralized with caustic soda, the hydrofluoric acid and then the excess of sodium acetate added and the gas introduced. True, I have as yet made no attempt to determine the amount of antimony present in the filtrate from the antimonious sulphide precipitated from such a solution, but the quantity must be practically negligible, for the figures for the tin and antimony found agree remarkably well with those representing the amounts taken.

The following experiment goes to show the degree of accuracy of this last mode of procedure: 0.4232 gram of recrystallized tartar emetic was placed in the large platinum dish and 25 cm^3. of the tin solution, 5 cm^3. concentrated hydrochloric acid and 5 cm^3. 48 per cent. hydrofluoric acid were added. The liquid was stirred with a platinum spatula until solution was complete, then diluted to 300 cm^3. and the hydrogen sulphide introduced. The antimonious sulphide was filtered off, dried, heated to blackness in a current of carbon dioxide and weighed according to the directions already given. The tin in the filtrate was also determined as above described.

Found: 0.1563 gram Sb = 36.94% and 0.1498 gram Sn = 99.87%.

The percentage of antimony in the sample of tartar emetic was next determined.

Tartar emetic taken. Gram.	Sb_2S_3 found. Gram.	Sb found. Gram.
0.51	0.2632	0.1880

0.1880 Sb = 36.86%.

It may be well to state that solutions of tin and antimony containing hydrofluoric acid can be diluted indefinitely without any basic compounds separating out.

The method is being thoroughly examined, especially as regards its applicability to the analysis of alloys and metallurgical products containing tin and antimony.

PRINCETON, N. J., Dec. 20, 1908.

DETERMINATION OF FERROUS OXIDE IN MAGNETITE.

BY R. B. GAGE.

Received Jan. 16, 1909.

The various errors that may occur in the determination of ferrous iron by the Mitscherlich method or those of Pratt and Cooke, their causes and the necessary corrections, are discussed by Hillebrand[1] so thoroughly that it is not necessary to deal with them all here. However, since that

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[1] *U. S. Geological Survey Bulletin, No.* 305 (1907), pp. 131–44.

caused by the action of the manganous salts on the permanganate is of special importance in certain cases studied by the writer it will be considered in the present paper.

While making a series of analyses of magnetites containing from 25 to 30 per cent. of ferrous oxide, the writer found it almost impossible to get good check results by any of the hydrofluoric acid methods unless the excess of this acid was expelled. To drive off this excess of acid lengthens the time of the determination very much, increases the chances of oxidation, and introduces other objectionable conditions. The large amount of manganese introduced into the solution during titration makes the end reaction exceedingly difficult to secure. In fact, an excess of 5 cc. of the oxidizer would only give a passing color.

The results secured by decomposing the ore with hydrochloric acid as recommended by some authorities are not only worthless in many cases, but the chlorine liberated soon ruins the platinum crucible. Only in the case of those ores which are known to contain no manganese in the dioxide state and are completely decomposed by hydrochloric acid, is it safe to determine the ferrous iron by this method. Even then the results are not always above suspicion.

A few drops of permanganate added to a solution containing as much as 10 cc. of hydrofluoric acid will give a fairly permanent color, but if some manganous sulphate is added the color will disappear at once. If the substance under examination does not contain over 5 per cent. of ferrous oxide, the amount of permanganate required to oxidize it will not introduce enough manganese into the solution to obscure the end point to any marked degree. But as the ferrous oxide increases, the end point becomes more and more difficult to secure.

This reduction of the permanganate after the iron has all been oxidized is caused by the action of the manganous fluoride. When vanadium is present it also will reduce some permanganate at this point, as vanadium oxidizes much slower than iron.

If the solution could be freed of hydrofluoric acid or the same rendered inert, there is no reason why the ferrous oxide could not be determined with as great a degree of accuracy in substances rich in this oxide as in those that contain but little of it.

It was found that the error caused by the excess of hydrofluoric acid in the solution could be decreased very much by adding sufficient calcium phosphate to the solution just before titrating to precipitate the fluorine as calcium fluoride. This renders the fluorine quite inert and the end point is fairly permanent. An excess of the calcium phosphate over what is required to precipitate the fluorine should always be added. When working on a half gram of material, five grams of calcium carbonate converted into the phosphate will be sufficient unless little or no hydrofluoric acid was expelled during solution of the material. When this happens, more of the calcium phosphate should be used.

A series of ten determinations were run on a sample of magnetite and the results secured are given below. The first five were made in the usual manner while the calcium phosphate was used in the last five. A half gram of material was used in each determination. Each cubic centimeter of permanganate represents 0.0025 gram of iron.

	Without Ca phosphate.			With Ca phosphate.	
No.	$KMnO_4$ required. cc.	Per cent. of FeO.	No.	$KMnO_4$ required. cc.	Per cent. of FeO
1	41.6	26.74	6	41.1	26.43
2	41.3	26.55	7	41.0	26.37
3	41.5	26.67	8	41.0	26.37
4	41.2	26.49	9	41.1	26.43
5	41.3	26.55	10	41.0	26.37

It is also a question whether anything is gained by reducing the material to an impalpable powder. In fact the material seems to cake quicker in the bottom of the crucible when exceedingly fine while little or no time is saved in decomposing it. It has also been shown that more or less oxidation of the ferrous iron takes place during this fine grinding.[1] Material that does not contain grains larger than 0.08 mm. in diameter can usually be decomposed in about 5 minutes.

The method and apparatus used in the New Jersey Geological Survey laboratory to decompose the material are similar to that recommended by Pratt with a few modifications and are described below.

A 50 cc. platinum crucible with a tight fitting lid is a very convenient size for this determination. A piece of thick card asbestos having an opening in the center that will allow the crucible to pass about half way through is also required. This opening should form as nearly an air-tight opening as possible. A loop is made on the end of a stiff platinum wire, the diameter of the same being slightly larger than that of the opening in the asbestos board, so it will fit the crucible a little above the point where the crucible rests in the asbestos board. The wire is bent perpendicular to the plane of the loop and should extend about two inches above the crucible when the latter rests in the loop.

A half gram of the sample is weighed into the crucible. It should be thoroughly moistened with water and a couple of coils of fine platinum wire added to prevent bumping. The crucible is hung in the loop of platinum wire and lowered into the opening in the asbestos board. A cold mixture of 10 cc. of hydrofluoric acid and 15 cc. of dilute sulphuric acid (1 : 3) is added and the crucible quickly covered. A 6-inch funnel, the top of which is connected with a CO_2 generator and the inside paraffin coated, is placed over the crucible. In case the funnel does not fit the

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[1] THIS JOURNAL, 30, 1120.

asbestos board tightly, a little water poured around its base from time to time will keep the joint quite air-tight. If the generator is working vigorously, the enclosed air will be expelled in a few minutes. The chances of oxidation during this time are exceedingly small because the sample is attacked but little by the cold acid mixture. After the air has been expelled from the funnel, a Bunsen burner is placed beneath the crucible, the top being about three inches below its bottom. The flame is raised until it nearly touches the crucible and kept at this height until the contents have come to a boil, when it is lowered just enough so the liquid will continue to boil gently. If the heat is not sufficient to keep the material in motion, the heavy mineral particles may settle to the bottom of the crucible and escape decomposition. Also a much smaller per cent. of the hydrofluoric acid will be expelled than otherwise. On the other hand, if too much acid and water are driven off, some of the salts will be forced out of solution. A reddish-brown sediment in the bottom of the crucible that will dissolve when the solution is diluted should not be mistaken for undissolved material. An ordinary rock can usually be decomposed in five minutes. Magnetites and rocks rich in ferromagnesian minerals may take a little longer.

After the sample is completely decomposed, the burner is removed and when the steam in the crucible has condensed, the lid of the crucible is held firmly in place with a glass rod while the crucible is raised by the platinum wire and plunged at once into a beaker containing from 400–500 cc. of cool boiled distilled water. The lid is kept in place until the beaker is placed beneath the burette ready for titrating. The contents of the crucible are quickly mixed with the excess of cold water, a solution containing the required amount of calcium phosphate added and the titration executed as rapidly as possible. The first permanent color is taken for the end point, even if it does fade in a few moments. A few more drops should give a good color if the addition of the oxidizer was stopped at the right point and should always be added as a check. If the solution contains too much free sulphuric acid, no precipitate of calcium fluoride will appear on adding the calcium phosphate. The excess of acid used to decompose the material is sufficient for titrating while it is not enough to prevent the precipitation of the fluoride. It is not advisable to add the calcium phosphate before the contents of the crucible have been mixed with the large excess of cold water, as a dense precipitate may form in the crucible that might enclose some ferrous iron.

The writer has had little trouble in securing duplicate determinations that vary less than 0.1 cc. in a total consumption of 48 cc. of permanganate, the iron value of the same being 0.0025 gram of metallic iron per cc. A blank determination should always be run and the corresponding correction made.

To prepare the calcium phosphate solution, suspend five grams of calcium carbonate in 50 cc. of distilled water and add 10 cc. of ortho-phosphoric acid (85 per cent.) slowly while stirring.

GEOLOGICAL SURVEY, TRENTON, N. J.

RAPID ELECTRO-ANALYSIS WITH STATIONARY ELECTRODES.

BY JOHN T. STODDARD.

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In the interesting development, during the last few years, of methods for the rapid precipitation of metals by the electric current, the efficiency of cathodes of gauze, and of mercury with stationary anodes seems to have been largely overlooked. General attention was directed in 1903 to the fact that electro-analyses could be made in much less than the usual time by using stronger currents with rotating electrodes. Gooch and Medway[1] rotated the cathode, Exner,[2] the anode; and since that time much work has been published on the use of the rotating anode with dish, gauze, and mercury cathodes. The agitation of the solution, which is apparently the chief function of the rotating electrode, has also been accomplished by rotation of the solution while the electrodes are stationary—recently by Frary[3] through the clever use of a solenoid. Rotation has come to be regarded as the essential feature of rapid electro-analytical procedure.

The experiments described in this paper show that rotation is not essential; that similarly rapid results can be obtained with stationary electrodes and no agitation of the solution beyond that produced by the heating effects and gas-evolution caused by the strong currents employed.

I. The Gauze Cathode with Stationary Anode.

In July, 1899, Cl. Winkler[4] published a brief paper on "Die elektrolytische Metallfällung unter Anwendung von Elektroden aus Platindrahtgewebe" in which he stated that with a cathode of platinum gauze good deposits of a number of metals could be obtained when higher current densities than usual were employed; and that the time of precipitation was reduced to one-fourth of the usual time. The efficiency of the gauze was ascribed to the utilization of the entire surface and to the fact that the deposited metal closes on itself around each wire of the mesh, and thus adheres better than on a plane surface. Winkler records the use of a current of 0.5 ampere, and calculates the current density as

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[1] *Am. J. Sci.*, 4th Series, **15**, 320.

[2] THIS JOURNAL, **25**, 896.

[3] *Z. Elektrochemie*, **23**, 308 (1907).

[4] *Ber.*, **32**, 2192.