A MODIFICATION OF THE PERMANGANATE METHOD FOR THE DETERMINATION OF IRON.

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THE methods generally employed for the volumetric determination of iron, are the permanganate and Kessler's modification of the bichromate method. The general accuracy of these methods cannot be doubted and the only objection to them is the time that they consume. If potassium bichromate be used the titration may be made in the presence of hydrochloric acid, and stannous chloride can be employed as a reducing agent. The actual process of titration however is very tedious and in many cases is not as accurate as determinations by the permanganate method.

In using the old permanganate method, however, the solutions must be free from hydrochloric acid as potassium permanganate is decomposed by the acid in the presence of ferric salts. On this account the hydrochloric acid is usually driven off by evaporation with sulphuric acid, and the iron is afterwards reduced by zinc. This is at best a long and tedious process. If the hydrochloric acid is not driven off, the action of ferric salts must be prevented by the addition of some substance. The ferric salts seem to act catalytically,[1] for oxalic acid may be titrated in hydrochloric acid solution with potassium permanganate with perfect sharpness, and without a trace of chlorine being set free, showing that the decomposition of the permanganate is not due to the hydrochloric acid alone.

The catalytic action of the ferric salts may be very much diminished by the addition of other salts such as the sulphates of magnesium, zinc, and manganese, and several methods have been devised in which advantage is taken of this property of these salts. The use of manganous sulphate for this purpose was first proposed by C. Zimmerman[2]. He gives a number of analyses showing the agreement between the results obtained from the hydrochloric and the sulphuric acid solutions. Zinc was used as the reducing agent.

Reinhart[3] improved Zimmerman's method by using stannous

1 Ostwald's Foundations of Analytical Chemistry, p. 144.
2 *Ber. d. chem. Ges.*, *1884*, 15, 779.
3 *Stahl und Eisen*, 4, 704.

chloride as a reducing agent, removing any excess of the latter with mercuric chloride and adding sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid permits the formation of ferric phosphate, a solution of which is nearly colorless, and does not obscure the end-reaction as the yellow ferric chloride would otherwise do.

C. T. Mixer and H. W. DuBois[1] modified this method slightly and gave a number of analyses showing the close agreement between the results obtained by this and by other methods.

The electric conductivity of solutions of the mercuric halides shows that they are ionized to an extremely slight extent, while the mercuric salts of oxygen acids are dissociated normally.

Since compounds of slight ionization always result when their constituent ions meet, mercuric halides are invariably formed when a mercuric salt of an oxygen acid is added to a solution containing halogen ions. If an excess of the salts of the oxygen acid be added the presence of the mercury ions derived from its dissociation, will diminish the already very slight ionization of the mercuric halogen compound, until it is practically nothing. Hence the solution would contain no halogen ions. As is well known there must be dissociation or the formation of ions before a chemical reaction can take place, and under the conditions above mentioned there will be no formation of halogen ions, hence such a solution will show none of the characteristic reactions of the halogens.

As an illustration of the foregoing, it may be noted that silver nitrate will give no precipitate in a dilute solution of a chloride in the presence of an excess of mercuric sulphate, and also that silver chloride is moderately soluble in a solution of mercuric sulphate.

From these general principles we concluded that it ought to be possible to titrate iron with permanganate in the presence of hydrochloric acid if an excess of mercuric sulphate be added to the solution. A number of experiments to test this conclusion were then made, with very satisfactory results.

In order to compare the results obtained in hydrochloric and in sulphuric acid solutions the following experiments were tried:

1 This Journal, 17, 405.

Five grams of ammonium ferrous sulphate dissolved in 500 cc. of water and 100 cc. of this solution were used for each titration.

		Per cent. of iron.	
		Found.	Theory.
No. 1.	Sulphuric acid alone............14.21		14.28
No. 2.	" " " 14.21		14.28
No. 3.	" " " 14.28		14.28
No. 4.	Sulphuric acid with 5 cc. hydrochloric acid, and mercuric sulphate..14.21		14.28
No. 5.	Sulphuric acid with ten cc. of hydrochloric acid and mercuric sulphate..........................14.28		14.28

In order to determine whether this process would be applicable where stannous chloride was used as a reducing agent, a number of tests were made upon ammonium ferric alum, and in these determinations and for all subsequent analyses the following solutions were employed.

Solution A.—A five per cent. solution of stannous chloride. This solution need not necessarily be freshly prepared, but a portion of it should give no precipitate when diluted with twenty times its volume of water and boiled. The solution may be kept in good condition by acidifying with hydrochloric acid and putting a few fragments of tin into the bottle.

Solution B.—Hydrochloric acid, of a specific gravity 1.10, made by mixing equal volumes of acid of specific gravity 1.20 and water.

Solution C.—A mercuric sulphate solution. This is made by adding to 200 grams of mercuric sulphate eighty cc. of sulphuric acid (conc.) and adding this paste to 800 cc. of water. (If a yellow precipitate of basic mercuric sulphate is formed add more sulphuric acid.) To this is added 100 grams of orthophosphoric acid, dissolved in a little water and the whole is diluted to one liter.

If a good quality of mercuric sulphate is not at hand the salt may be easily prepared by heating metallic mercury in a porcelain evaporating dish on a sand-bath, with one and a half times its weight of concentrated sulphuric acid, as long as fumes of sulphuric acid are given off or till a sample of the salt does not become moist on exposure to the air. The mercuric sulphate should be tested by dissolving a portion of it in water, acidulated with sulphuric acid, and adding hydrochloric acid. If a

precipitate is produced the salt must be reheated with sulphuric acid.

METHOD I.

A process of analysis that we have found to be convenient is to dissolve the substance in water with a varying quantity of hydrochloric acid and heat to boiling after diluting to 100 cc., reducing with stannous chloride, adding small portions at a time until the solution becomes colorless, and a droplet gives no coloration with potassium thiocyanate.   In order to oxidize any excess of stannous chloride that may have been used, a solution of potassium permanganate is added drop by drop until a droplet of the iron solution gives a faint but distinct color with potassium thiocyanate; stannous chloride, not more than one or two drops, is then added very cautiously.   This whole process should be carried on at a boiling heat.   The solution is then cooled and fifty cc. of dilute sulphuric acid is added, and for every ten cc. of hydrochloric acid that has been used, add thirty-five cc. of the mercuric sulphate solution, dilute to 400 cc., and titrate with potassium permanganate as usual.   If the process of reduction has been properly carried out there will be only a slight precipitate of mercurous chloride formed from the reducing action of the stannous chloride, but if any great excess of stannous chloride has been added a heavy white precipitate will result and in such cases the determination cannot be relied upon.

METHOD II.

The substance is dissolved, best in a small Erlenmeyer flask in fifteen cc. of hydrochloric acid (solution B), two cc. of mercuric sulphate (solution C) is added, the whole is heated to boiling, and stannous chloride is added in small quantities at a time.   The precipitate that may be temporarily produced as each drop of the stannous chloride is added, will dissolve after boiling a few seconds, until all the iron is reduced, when the solution becomes colorless, and the addition of a single drop of stannous chloride produces a perceptible turbidity or a precipitate, which does not redissolve on boiling.   This shows the end of the reduction.   The contents of the flask is rinsed into a beaker and diluted to about 300 cc., fifty cc. of dilute sulphuric acid are added, and then forty-five cc. of the mercuric sulphate (solution

C). The solution is then ready for titration without cooling as the amount added should cool it sufficiently.

Method I can be used in all cases, while Method II (which is much shorter), can always be used where there is not too much insoluble residue, which might obscure the reaction at the end of the reduction.

ANALYSIS OF AMMONIUM FERRIC ALUM BY METHOD I.

	Per cent. of iron found.	Oxygen = 15.8. theory.
No. 1. .... 11.64		11.62
No. 2. .... 11.66		....
No. 3. .... 11.68		....
No. 4. .... 11.61		....
Average of 10 others.................. 11.67		....

ANALYSIS OF AMMONIUM FERRIC ALUM BY METHOD II.

No. 1. .... 11.74		....
No. 2. .... 11.74		....
By reduction with zinc in a sulphuric acid solution.		
No. 1. .... 11.74		....
No. 2. .... 11.74		....

The results obtained by Method II would naturally be higher than those by Method I on account of the removal of a little iron in the process of testing in the latter case.

APPLICATION OF THE PROCESS TO IRON ORES.

In the analysis of ores, if the material be soluble in hydrochloric acid, it is boiled for some time with ten to fifteen cc. of solution B, until completely decomposed. The addition of some of the stannous chloride solution to the hydrochloric acid hastens the process of decomposition. When the ore is completely decomposed, if Method I is to be followed, the solution is diluted to 100 cc. and reduced as described under the above head. If Method II is to be followed, which is usually the better, the solution is not diluted but the two cc. of mercuric sulphate is added at once and the process continued as described. If long boiling was required for the decomposition of the ore, the greater part of the hydrochloric acid may have been driven off. Under these conditions the precipitate formed by the addition of a small quantity of stannous chloride will not readily redissolve, even when considerable ferric salts remained in the solution. In

such a case a few more cubic centimeters of hydrochloric acid should be added. Ores not soluble in hydrochloric acid may be dissolved after fusion with potassium hydrogen sulphate and then reduced by either method.

RESULTS.

Name.	Iron found. Per cent.
Limonite, No. 1	35.08
" "	35.02
Limonite, No. 2	54.37
" "	54.49
" "	54.49
Limonite, No. 3	37.47
" "	37.43
Limonite, No. 4	36.68
" "	36.68
" "	36.72
Magnetite,	71.87
"	71.64
"	71.64
"	71.87

In the analysis of the magnetite the determination was made upon a small quantity of the ore, three-tenths gram in each case, so any slight error in reading the burette was increased. The analyses of the limonites Nos. 3 and 4 were made by two different persons independently, and in each case they were entirely unfamiliar with the process, and good results were obtained without practice. This shows these modifications are easily mastered, and not difficult of execution.

The solution of mercuric sulphate described above contained one gram of the salt in five cc., and since four grams of mercuric sulphate are required to completely non-ionize one gram of hydrochloric acid, it is evident that thirty-five cc. of the mercuric sulphate solution will not be sufficient for all the chlorine in ten cc. of hydrochloric acid (sp. gr. 1.10) ; but much of the hydrochloric acid will escape during the process of dissolving the ore, and experience has shown us that thirty-five cc. of the mercuric sulphate solution is sufficient to combine with the chlorine that is left.

If too little mercuric sulphate has been added, the solution will smell of chlorine after the addition of permanganate. On the other hand a very great excess of mercuric sulphate will lower

the ionization of the mercuric chloride until it becomes lower than that of the mercurous chloride (formed by the reducing action of stannous chloride), and then the latter will dissolve, forming mercuric chloride and mercurous sulphate.   Since mercurous sulphate exerts a reducing action on permanganate, this will introduce an error into the determination. Our experiments have shown that anywhere from twenty-five to fifty cc. of mercuric sulphate solution to ten cc. of hydrochloric acid, will give accurate results in the presence of small quantities of mercurous chloride.

The points requiring special care in this process then are :

1. Use stannous chloride that is in good condition.

2. Have the smallest possible excess of stannous chloride present after the reduction is completed.

3. Carefully adjust the proportions between the mercuric sulphate and the hydrochloric acid.

The speed of this process leaves nothing to be desired.   Less than three minutes, in the case of soluble salts, has been found sufficient time for solution, reduction, and titration.

In conclusion we wish to acknowledge our indebtedness to Prof. E. H. S. Bailey for his advice and many valuable suggestions during the progress of the work.

A NEW APPARATUS FOR SULPHUR DETERMINATIONS IN IRON AND STEEL AND A USEFUL FORM OF WASH-BOTTLE.

By Richard K. Meade.

THE writer has found the two forms of chemical apparatus mentioned below of much use in his work and describes them here, in the hope that they may prove of equal service to other analysts.   The first description is that of an apparatus to be used in the determination of sulphur in iron and steel, by the method of conversion into hydrogen sulphide and absorption of the evolved gas, in an alkaline solution of lead nitrate.

The apparatus is shown, drawn to one-eighth scale, in Fig. 1.   It consists of the following parts :

1. A half liter flask, of the "Joliet" pattern, such as is used in the laboratories of iron and steel companies.   The flask is