XLIII.—*On a Method of Precipitating Manganese entirely as Dioxide, and its Application to the Volumetric Determination of Manganese.*

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MANY methods of determining manganese volumetrically have been from time to time suggested by various chemists, but none have, as yet, come into general use, although a ready means of quantitatively determining this metal has been much needed in metallurgical laboratories since alloys of manganese have been so largely employed in the manufacture of steel. For the most part these proposed methods have been based on obtaining the manganese in a known and definite state of oxidation, and, after determining the amount of oxygen in the oxide over and above that which exists as monoxide, to calculate therefrom the amount of manganese. Some of these methods have failed because, in practice, it has been found that they are more troublesome than the gravimetric methods they were intended to supersede; but, I have no doubt, most have failed from the difficulty or impossibility of obtaining the whole of the manganese in the necessary definite and uniform state of oxidation.

M. Pereño has described (*Ann. Chim. Phys.* [5], 11, 571—574) a method of determining manganese in manganiferous iron ores, in which a weighed quantity of the ore is calcined for the purpose of converting the whole of the manganese into manganoso-manganic oxide (Mn_3O_4), and afterwards determining, by Bunsen's method, the amount of chlorine produced on heating the oxide with hydrochloric acid. This method, in my hands, with the utmost care, has yielded very irregular results, making an ore containing 20 per cent. of manganese to indicate amounts varying from 17 to 25 per cent. of manganese. These variations are due to the irregular oxidation of the ore during the calcination, and I consider the method altogether untrustworthy on this account.

Lenssen's method—adding the solution of manganese mixed with a ferric salt to a boiling alkaline solution of potassium ferricyanide, and afterwards determining the amount of dioxide formed—as described in the latter editions of Fresenius' "Quantitative Analysis," has also given me irregular results, in one instance only 81 per cent. of the manganese being precipitated as dioxide.

Messrs. Wright and Luff have recently shown ("Report on Researches on some points in Chemical Dynamics," *Journal of the Chemical Society*, vol. 33, page 513) that certain methods usually prescribe for producing hydrated manganese dioxide do not yield this

oxide alone, but a mixture of dioxide with lower oxides of manganese; thus, the precipitate formed by adding caustic soda to a solution of pure manganous chloride and afterwards digesting for 48 hours in excess of bromine, was found by them to consist of oxides in which 82·46 per cent. of the manganese existed as dioxide, and 17·54 per cent. as monoxide, or oxides equal to these, and that the precipitate formed by boiling potassium permanganate solution with dilute nitric acid was, similarly, found to consist of oxides in which 85·64 per cent. of the manganese existed as dioxide and 14·36 per cent. as monoxide.

I have carefully tried other methods usually recommended for obtaining manganese dioxide from a solution of monoxide. On adding excess of solution of calcium hypochlorite (bleaching powder) to a solution of pure manganous chloride and heating, the whole of the manganese is precipitated, not all, however, as dioxide, but as a mixture of this oxide with lower oxides. In one instance the precipitate thus formed contained 97·5 per cent. of its manganese as dioxide, and in another 98·5 per cent.

Kämmerer and Waage's methods of precipitating manganese from an acetic acid solution by means of bromine, chlorine, and calcium or sodium hypochlorite, were also frequently tried, but it was always found that not more than from 95 to 99 per cent. of the manganese could be obtained as dioxide.

Numerous modifications of these and other methods were tried, but all failed to precipitate the manganese wholly in the desired state of oxidation.

The precipitates of hydrated manganese oxides obtained by these methods were tested for the amounts of dioxide they contained by adding them to a carefully measured quantity of solution of ferrous sulphate containing excess of sulphuric acid, and afterwards determining the amount of unoxidised ferrous sulphate remaining by a standard solution of bichromate of potash.

The above-named experiments were made with weighed portions of pure manganoso-manganic oxide (Mn_3O_4) carefully prepared from very pure crystals of manganous sulphate in the following manner. The manganese in a solution of the manganous sulphate was precipitated by ammonium sulphide, the precipitate washed to free it from a slight trace of lime it contained, redissolved in hydrochloric acid and precipitated as manganous carbonate by ammonium carbonate. After washing the precipitate until it was free from chlorides, it was ignited at a high temperature in a muffle furnace until it ceased to change in weight. The purity of the Mn_3O_4 was carefully tested by precipitation with bromine, and also by determining the amount of excess of oxygen over MnO it contained.

After numerous experiments it was at last found that the whole of the manganese in a manganous chloride solution could invariably be precipitated in the condition of dioxide, *if a certain amount of ferric chloride be also present in the solution*, when a sufficient excess of solution of calcium hypochlorite or bromine-water is added, and, after heating the solution to from 140° to 160° F. (60° to 70° C.) excess of calcium carbonate is then added, and the mixture well stirred.

When the ferric salt is absent and the other conditions are observed, that is, when excess of solution of calcium hypochlorite or bromine water is added to a solution of pure manganous chloride, then, after heating to about 150° F., adding excess of calcium carbonate and stirring, the precipitate invariably contains a certain proportion of lower manganese oxides, the amount of manganese precipitated as dioxide varying from 98·20 to 99·27 per cent. of the amount of manganese present in the solution.

It is difficult to understand why ferric oxide should have this effect on the condition of the manganese precipitate under the circumstances described. Probably in the absence of iron a portion of the manganese is precipitated in a lower state of oxidation as manganite or manganese, but when ferric oxide is present, it takes the place of the basic manganese.

Heat is also essential in order to obtain all the manganese as dioxide, for if the precipitation is made by calcium hypochlorite and calcium carbonate in the presence of much ferric chloride *in the cold*, the precipitate then contains only from 98 to 99 per cent. of its manganese as dioxide.

I have also experimented carefully to ascertain the amount of ferric chloride necessary to cause the whole of the manganese to be precipitated in the desired condition of dioxide, and I find that if there is at least half as much iron as manganese present in the solution, it is sufficient. In practice, however, I prefer to have about equal quantities of each metal in solution. A large excess of iron is no disadvantage.

When equal quantities of manganese and iron are present, and the other conditions fulfilled as described, I have found, by numerous experiments, that the whole of the manganese is precipitated as dioxide, the results I have obtained having almost invariably indicated from 99·95 to 100·12 per cent. of the manganese precipitated in this form when operating on portions of from 3 to 6 grains of pure manganoso-manganic oxide.

In order to ascertain if alumina had the same effect as iron on the character of the precipitate, a solution of alum was added to a known weight of manganese, and treated in the manner above described. Only 98·6 per cent. of the manganese was precipitated as dioxide.

Barium chloride was also tried in the same way, but only 99.18 per cent. of the manganese was precipitated as dioxide in this case. Neither aluminium nor barium salts have therefore the same effect as ferric chloride.

I will now describe the manner in which I use the above mentioned reaction for the quantitative determination of manganese, and this will be done best by giving the details of my method in its application to the testing of manganiferous iron ores, spiegeleisen, ferro-manganese, steel, &c., for manganese.

The following are the special solutions and other special reagents required in the process. These are all in ordinary use in metallurgical laboratories, or can be readily obtained. They are :—

1st. *Solution of calcium hypochlorite (bleaching powder).*—The solution I use is made by diffusing in 10,000 grains of water 150 grains of ordinary bleaching powder or chloride of lime, containing about 35 per cent. of available chlorine. The clear solution is separated from the insoluble portion by decantation or filtration and bottled for use.

2nd. *Calcium carbonate.*—It is desirable that this should be of a light granular pulverulent character, so that it can be readily diffused through the solution and does not form clots which fall at once to the bottom of the beaker in which the precipitation takes place. This kind of carbonate of lime can often be had from the dealers in reagents; but it may be formed when solutions of calcium chloride and sodium carbonate are added together at a temperature of about 180° F., keeping the calcium chloride slightly in excess, and washing the precipitate well and drying.

3rd. *Solution of ferrous sulphate in excess of sulphuric acid.*—The solution I use contains about 10 grains of iron in 1,000 grains of solution, and is made by dissolving crystals of ferrous sulphate in a mixture of one part of monohydrated sulphuric acid, and three parts of water. 530 grains of crystals in 10,000 grains of the dilute acid give a solution containing about 10 grains of iron in each 1,000 grains.

4th. *Standard solution of potassium dichromate.*—The solution I use is made so that 1,000 grains of it are equal to 10 grains of iron, and is the solution I use in the determination of iron in iron ores, &c. It should be carefully standardised.

Manganiferous Iron Ores.

These ores usually contain from 15 to 25 per cent. of manganese, and at least 20 per cent. of iron; they therefore usually contain an amount of iron sufficient for the dioxide precipitation. 10 grains of the ore, dried at 212° F., are placed in a beaker of about 20 oz.

capacity and dissolved, by the aid of heat, in about 100 fluid grains of hydrochloric acid of about 1.180 sp. gr. When completely dissolved, the cover and sides of the beaker are rinsed by a jet of cold water, and then calcium carbonate is added until the solution becomes of a slightly reddish colour, showing that the free acid is neutralised. Six or seven drops of hydrochloric acid are now added in order to slightly acidify the solution, as it is found that the precipitate falls in the best condition for being filtered and washed when this is done. About 1,000 grains of the solution of bleaching powder are now added, and then boiling water is run in until the solution is heated to about 140 to 160° F. The point when the right temperature has been reached may be ascertained with sufficient accuracy by applying the hand. About 25 grains of calcium carbonate (which, for convenience, may be measured) are now added, and the solution well stirred until the evolution of carbonic acid ceases. The dark-brown precipitate of oxides of manganese and iron settles readily, generally leaving a colourless supernatant liquid, but if the bleaching powder has been much in excess the supernatant liquid has sometimes a pink colour, owing to the formation of permanganic acid. Should this be the case a few drops of alcohol are added until the pink colour is destroyed. If sufficient bleaching powder has been added, the solution smells of chlorine, or it may be tested for excess by a strip of iodised starch paper.

Instead of the solution of bleaching powder, about 500 grains of saturated bromine-water may be used. In this case it is unnecessary to add any acid after the neutralisation of the solution by calcium carbonate, as sufficient acid is formed in the reaction. Care must be taken that sufficient calcium carbonate is present to neutralise all free acid at the end of the precipitation.

The precipitate is now collected on a double filter of sufficient capacity, and washed with cold or warm water until the washings show no trace of chlorine or bromine when carefully tested by iodised starch paper. The washing is readily accomplished and rarely takes longer than a quarter of an hour.

1,000 grains of the acidified ferrous sulphate solution are now carefully measured from a pipette into the beaker in which the precipitation has been made, and which usually contains a small quantity of adhering dioxide, and the filter with its contents is removed from the funnel and placed in the iron solution. The precipitate very readily dissolves even in the cold solution, the manganese dioxide converting its equivalent of ferrous sulphate into ferric sulphate. A sufficient amount of cold water is now added, and the amount of ferrous sulphate still remaining in the solution is ascertained by adding from a burette the standard solution of potassium dichromate just as in the testing of an iron ore.

The exact amount of ferrous sulphate existing in the 1,000 grains of ferrous sulphate solution at first is determined by measuring another 1,000 grains from the pipette, and, after adding a filter to it of the size used in collecting and washing the precipitate, titrating it with the potassium dichromate solution. Sometimes filtering paper has a slightly reducing action, and the influence of this is thus counteracted. It is, however, quite easy to obtain filtering paper that has no reducing action on the solution; but it is safer to standardise after adding a filter to the solution as I have directed.

Supposing the 1,000 grains of ferrous sulphate solution used in standardising has required 101.1° of dichromate solution (I use a burette graduated to hold 150° of 10 grains each, or 1500 grains) and the 1,000 grains to which the manganese precipitate obtained in testing an ore has been added has required 57.0° of the dichromate solution, the percentage of manganese in the ore is calculated as follows: $101.1 - 57.0 = 44.1^\circ$ of dichromate solution, which are equal to 4.41 grains of iron, the amount of iron converted from ferrous to ferric sulphate by the manganese dioxide yielded by 10 grains of the ore. On multiplying the amount of iron thus peroxidised by 0.491 the total amount of manganese contained in the ore is ascertained. In this case $4.41 \times 0.491 = 2.165$ grains of manganese in the 10 grains of ore, equal to 21.65 per cent.

Should the ore to be tested be a rich manganese ore containing less iron than one half of the manganese it contains, it will then be necessary to add a sufficient amount of ferric chloride free from manganese. As before mentioned, I prefer having about equal parts of manganese and iron in solution when the precipitation is made. The ferric chloride I use for this purpose, and which was used in the above-mentioned experiments with pure Mn_3O_4 , is prepared by precipitating the ferric oxide in a ferric salt once or twice with calcium carbonate, and washing so as to get rid of the small amount of manganese which even the purest iron wire contains. The ferric oxide is then dissolved in hydrochloric acid and made up to a known bulk.

For the amounts of bleaching powder solution and other reagents mentioned above, it will be necessary to operate upon such a quantity of the sample as will not contain much more than about 2.5 grains of manganese. If larger quantities are taken, then the amounts of the reagents must also be proportionately increased. But it is unnecessary to operate upon a larger quantity than I have indicated, seeing that with this quantity there is no difficulty in obtaining results which agree within a tenth of a per cent.; moreover the bulk of the precipitate from such a quantity, and the amounts of the solutions required, are convenient to work with.

If it is preferred, a larger quantity of the ore—say 50 or 100 grains

—may be dissolved, and the solution made up to a known bulk in a measuring flask, from which measured portions may be taken.

It is necessary to standardise the ferrous sulphate solutions about once a day, as it becomes slowly oxidised on exposure to air.

Spiegeleisen.

This alloy usually contains from 10 to 25 per cent. of manganese and, of course, a sufficient amount of iron for the dioxide precipitation. 10 grains are taken for analysis. This amount is dissolved in about 120 grains of hydrochloric acid with the aid of heat. About 50 grains of nitric acid are then added for the purpose of converting the ferrous into ferric chloride. After washing the cover and sides of the beaker with cold water, the excess of acid is neutralised by the addition of calcium carbonate until the solution has a reddish colour. 1,000 grains of the bleaching powder solution or about 500 grains of bromine-water are added, without previous addition of hydrochloric acid as in the case of ores. Hot water is then added to heat the solution to 140—160° F., and then about 25 grains of calcium carbonate, and the solution well stirred. The rest of the process is conducted as before described.

Ferro-Manganese.

For the quantitative analysis of this alloy an amount which contains from two to four grains of manganese may be taken. The solution is made as in the case of spiegeleisen. If the alloy contains less iron than manganese, ferric chloride is added so as to make the amounts of the two metals in the solution about equal.* The amount of bleaching powder solution to be added must depend upon the amount of manganese in solution, taking care to add about 400 grains of bleaching powder solution of the strength above-named for every grain of manganese present.

As in the case of ores, instead of weighing off separately the amounts required for each test, a larger quantity may be dissolved

* Since the above was written I have ascertained that F. Kessler recommends the use of zinc chloride for the purpose of preventing the formation of lower oxides than dioxide when manganese is precipitated from its solutions (*Zeitschr. Anal. Chem.*, 1879, 1—14). The method by which he proposes to utilise this reaction for the volumetric analysis of manganese, is, in my opinion, too troublesome and complicated for ordinary use; but I have tried the use of zinc chloride, instead of ferric chloride, as applied to my method of precipitation and analysis, and find it answers equally well, and that it is sufficient to have about as much zinc as manganese present in solution. In cases, therefore, where a sufficient amount of iron is not already present, an addition of zinc chloride may be substituted for the ferric chloride above recommended.

and peroxidised, and, after making up the solution to a known bulk in a measuring flask, the necessary quantities for the test measured out.

Steel.

50 grains of steel are dissolved, by the aid of heat, in about 350 grains of hydrochloric acid of about 1.180 sp. gr. The ferrous chloride thus formed is then converted into ferric chloride by the addition of about 90 grains of nitric acid of about 1.400 sp. gr. The solution is made in a beaker of about 35 oz. capacity. Calcium carbonate is then added until the solution is slightly red. 135 grains of calcium carbonate are now weighed or measured, and about one-half of this added to the solution. After the effervescence caused by the escape of carbonic acid has ceased about 400 grains of the bleaching powder solution are added, and then hot water to heat to about 150° F., and then the remainder of the calcium carbonate. If all the calcium carbonate is added at once the effervescence is so great that the substance is likely to froth over the edges of the vessel; and if the bleaching powder solution is added before any calcium carbonate has been added, the chlorine is likely to be expelled by the evolution of the carbonic acid. The calcium carbonate is, therefore, added at twice, and the bleaching-powder solution between the two additions. The precipitate is then thrown on a sufficiently large filter, and washed until free from any trace of chlorine. Although the precipitate is bulky it is very readily washed.

About 200 grains of the ferrous sulphate solution are standardised and the same quantity used for decomposing the manganese dioxide in the case of steels; but it is sometimes found necessary to add a little additional sulphuric acid, in order to dissolve the ferric oxide precipitate and the excess of calcium carbonate it may contain.

Manganese-Slags, &c.

These are treated similarly to the above, using for the analysis such a quantity as will not contain more than about 2.5 grains of manganese for the above-named amounts of reagents, and taking care to have a sufficient amount of ferric chloride in the solution when the manganese is precipitated.

Should lead, copper, nickel, or cobalt exist in the substance under examination, these must be separated before the manganese is precipitated, as they form higher oxides under the conditions of the precipitation, which oxides, like manganese dioxide, convert ferrous into ferric oxide. Fortunately, in most manganiferous iron ores and in

spiegeleisen, ferro-manganese and steel, none of these metals occur in such quantity as to appreciably affect the correct estimation of the manganese.

Not only is a great saving of time effected by the use of this process instead of the gravimetric process, but in many cases much more accurate results are obtained than by the latter process. This is especially the case in the determination of manganese in manganiferous iron ores, slags, or other substances containing lime and magnesia. When manganese is precipitated by bromine from an ammoniacal solution in the usual way, the precipitate carries down with it small quantities of probably every other base existing in the solution; so that before the exact amount of manganese can be ascertained it is necessary to separate and determine all these substances, and deduct their weight from that of the bromine precipitate. In practice it is usual to separate and determine the amount of baryta the precipitate contains; then to separate the amounts of ferric oxide, alumina, zinc oxide, &c., it contains, and deduct these from the weight of the bromine precipitate; but the lime and magnesia, which the precipitate is also very liable to contain, are not usually separated, and in this way, I think, the amount of manganese in manganiferous iron ores is frequently overstated, sometimes even to the extent of one and a-half per cent. In confirmation of this view the following experiment may be cited. A mixture of 7 grains of pure manganoso-manganic oxide, (Mn_3O_4), 4 grains of calcium carbonate, and 4 grains of magnesium carbonate, was dissolved in hydrochloric acid, and precipitated in the usual way with bromine in ammoniacal solution. The precipitate, after careful washing, drying, and igniting, so as to convert the manganese again into Mn_3O_4 , weighed 7.45 grains instead of 7 grains. Had 20 grains of an ore containing these proportions of manganese, lime and magnesia been thus treated, the analysis would have indicated 1.62 per cent. more manganese than the ore actually contained. The precipitate weighing 7.45 grains was afterwards dissolved in hydrochloric acid, and, after precipitating the manganese by ammonium sulphide, amounts of lime and magnesia nearly corresponding with the amount of excess were obtained from the filtrate by the usual processes of analysis. On the other hand, an artificial mixture made to imitate the composition of a natural manganiferous iron ore, and containing, besides 21.5 per cent. of manganese, various quantities of calcium and magnesium carbonate, &c., when tested by the volumetric method I have described, was found by two tests to contain 21.46 and 21.51 per cent. of manganese respectively. The method is therefore much more exact than the usual gravimetric method when testing manganiferous iron ores, slags, &c.

In testing spiegeleisen and ferro-manganese, which do not contain

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