THE USE OF AMMONIUM PERSULPHATE IN THE DETERMINATION OF CHROMIUM IN STEEL.[1]

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AMMONIUM persulphate is used as a reagent for oxidizing chromium in steel in a method described by F. Ibbottson and R. Howden.[2] After oxidation the chromium is precipitated as lead chromate, filtered and determined volumetrically.

The writer has been using a method for some time in which the same salt is used, advantage being taken of the fact that in the presence of sufficient silver nitrate both the chromium and manganese are completely oxidized and can be determined volumetrically without previous precipitation. The method as outlined is applicable for ordinary chrome steels but not for tungsten or molybdenum steels, as some of these steels contain a carbide of chromium insoluble in sulphuric acid. This difficulty can be overcome by filtering the insoluble carbide, burning and fusing with a small amount of sodium carbonate and adding to the main solution. This, however, would prolong the operation but would still be an advantage over the methods now in use.

METHOD.

Weigh 1.25 grams of the sample into a No. 3 Griffin beaker, add 35 cc. dilute sulphuric acid (1 : 5), warm until the sample is in solution and add a small amount of ammonium persulphate to oxidize the iron and carbonaceous matter; dilute to 100 cc. and add 40 cc. silver nitrate solution (0.16 gram of the salt), now add an excess of ammonium persulphate (5 to 7 grams) and heat to boiling. Boil about five minutes to destroy excess of persulphate, cool and transfer to a 500-cc. calibrated flask, dilute to mark with water and mix thoroughly.

Pour 100 cc. (0.25 gram) into a 100-cc. calibrated flask; the remaining 400 cc. (1 gram) are transferred to a beaker, a measured volume of ferrous sulphate added and the excess titrated with a standard solution of permanganate until a pink color is obtained.

The number of cubic centimeters of the permanganate solu-

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[1] Read before the Pittsburg Section, October 19, 1905.

[2] *Chem. News*, **90**, 320.

tion used, subtracted from the number required for the volume of ferrous sulphate added, will give the volume of permanganate used by the chromium and manganese.

The contents of the 100-cc. calibrated flask are transferred to a porcelain dish and titrated with a standard solution of sodium arsenite until the color is bright yellow. The number of cubic centimeters of the arsenite solution used, multiplied by the value of the solution in manganese, will give the amount of manganese present.

The volume of permanganate used by the chromium is found by calculating the amount of manganese found to the equivalent number of cubic centimeters of the permanganate solution and subtracting this number from the volume of the permanganate used by the chromium and manganese. The number of cubic centimeters found to be used, multiplied by the value of the permanganate in chromium, will give the amount of chromium present.[1]

REAGENTS.

Sulphuric Acid.—A mixture of one part concentrated acid and five parts water.

Silver Nitrate.—Four grams of the salt are dissolved in one liter of water.

Ammonium Persulphate.—The salt should be slightly moist.[2]

Sodium Arsenite.—The solution is prepared as recommended by Blair.[3] The solution is standardized with a chrome steel of known manganese content so that the direct reading will give the per cent. of manganese. Mixtures of pure chromium and manganese solution may also be used.

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[1] EXAMPLE.—Let us assume that the chromium value of each cubic centimeter of the permanganate solution equals 0.001 gram and the manganese value 0.000633 gram; now if 50 cc. of the ferrous sulphate solution equals 49 cc. of the permanganate solution and the sample after oxidation and addition of 50 cc. of the ferrous sulphate solution requires 13 cc. of the permanganate solution, then 49 cc. minus 13 cc. equals 36 cc. or amount used by chromium and manganese.

If the sample should show 0.38 per cent. manganese by the arsenite titration, then 0.0038 divided by 0.000633 equals 6 or the number of cubic centimeters of permanganate solution equivalent to the per cent. of manganese found.

36 cc. minus 6 cc. equals 30 cc. × 0.001 gram equals 0.03 gram or 3 per cent. chromium.

[2] The dry salt, or one which has been dried at 120°, sometimes gives a good reaction, but at other times we have failed to secure satisfactory results, while good results have always been obtained with the moistened salt. Others have had the same experience. Such a difference seems, on the face of it, absurd, and this statement is made only as an empirical fact which has no apparent reason.

[3] "Chemical Analysis of Iron," fifth edition, p. 121.

Permanganate Solution.—The solution is made by dissolving 1.82 grams of pure potassium permanganate in 1 liter of water.

Ferrous Sulphate Solution.—The solution is made by dissolving 22.5 grams ferrous ammonium sulphate in water, adding 50 cc. strong sulphuric acid and diluting to 1 liter.

It is unnecessary to have this exactly equal the permanganate solution as a constant volume is used and the solution loses in strength. It is only necessary to find the volume of permanganate equivalent to the volume of ferrous sulphate used and this should be done every day.

The permanganate may be standardized by getting the iron value or by the use of a pure chromium salt. If the solution is standardized against iron the chromium value is found by the equation

167.7 : 52.1 :: iron value : x equals chromium value, and the manganese value by the equation

279.5 : 55 :: iron value : x equals manganese value.

If the solution is standardized with a pure chromium salt the manganese value is obtained by the equation

260.5 : 165 :: chromium value : x equals manganese value.

REMARKS.

In case the samples should run high in chromium the ferrous sulphate solution could be made stronger.

The permanganate solution should be allowed to stand several days before standardizing.

In case an appreciable amount of vanadium is present in a sample it will be necessary to determine the manganese by the bismuthate or Ford's method.

In using the method for tungsten steels some tungstic acid separates, but this does not seriously interfere with the titration.

The following results were obtained on some chrome steels and pure solutions of iron, chromium and manganese.

Number.	Chromium taken. Per cent.	Found. Per cent.	Manganese taken. Per cent.	Found. Per cent.
1	4.00	3.98	0.08	0.09
2	4.80	4.82	0.40	0.40
3	1.56	1.53	0.24	0.23
4	3.60	3.57	0.80	0.81
5	5.10	5.12	0.50	0.49
6	8.00	8.03	0.32	0.32

Steels.	Chlorate method.		Persulphate method.	
	Chromium.	Manganese.	Chromium.	Manganese.
1	1.50	0.35	1.51	0.36
2	2.88	......	2.85	0.14
Tungsten	3.50	0.12	3.49	0.13
Molybdenum	5.69	0.81	5.71	0.83

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REVIEW.

SOME RECENT WORK IN ORGANIC CHEMISTY.

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A review of the progress of organic chemistry must, of necessity, be a partial one. The greater part must be left untold. In preparing the following survey of the articles published by foreign investigators during the year 1904, I have chosen a few of the many interesting articles, and have been compelled, for lack of space, to exclude many which deserve mention. I hope that the ones which I have selected may be of general interest to those who are familiar with the methods and theories of organic chemistry.

During the year 1904, Grignard's reaction has been applied in a great variety of new syntheses, and seems to be at the begining, instead of at the end, of its usefulness. Gomberg's triphenylmethyl is still an unsolved riddle. The investigations of Fischer and of Curtius which have led to the building up of so many complex polypeptides, are giving us quite substantial assurance of future success in the synthesis of natural proteins. The study of quadrivalent oxygen derivatives has been continued, and has led to the preparation of many interesting oxonium compounds. The use of powdered nickel in the presence of hydrogen at temperatures above 100° for the purpose of reduction seems to be a method of great promise which may be applied for the reduction of many classes of organic substances. On the whole, the year has given us nothing which is strikingly new, but much that is of interest and importance.

Hydrocarbons.—Some interesting results have been obtained by the slow combustion of certain hydrocarbons. Bone and Wheeler (*J. Chem. Soc.*, **83**, 1074 (1903)), in a previous article, showed that methane gave first formaldehyde and water, and,