

MODIFIED WILLIAMS METHOD FOR MANGANESE.

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THE Williams method, as outlined in Blair's "Chemical Analysis of Iron," although a very accurate one, is unsatisfactory on account of the time required for the filtration of the precipitated manganese dioxide, which, together with a frequently occurring mass of gelatinous silica, chokes up the asbestos filter and makes the operation more or less tedious.

The following modification has been found to overcome this difficulty entirely, and its adoption has reduced the time of a determination very materially, by eliminating the uncertainty attendant upon the filtration of the slimy manganese dioxide.

METHOD.

Place 5 grams of pig-iron drillings in a No. 5 Griffin's beaker, with cover glass, add 75 cc. nitric acid (sp. gr. 1.20), and after violent action has ceased add approximately 10 cc. hydrofluoric acid. Give the beaker a circular motion to mix contents, and evaporate down until ferric oxide begins to separate out. Cool, add 100 cc. nitric acid (sp. gr. 1.42), and heat to boiling. Drop in a spoonful of asbestos fibers and then add approximately 7 grams potassium chlorate. Boil until green fumes disappear and nitric acid begins to volatilize. Remove from source of heat, cool rapidly, and filter the manganese dioxide precipitated on the suspended asbestos fibers, on a special filtering tube. Wash twice with strong nitric acid, and rinse out the beaker in which the precipitation was made with cold water, pouring the rinsings through the filter-tube. Continue the rinsing and washing until, when tested with litmus, no acidity is shown. Push the asbestos pad and precipitate back into the beaker, wash down the sides of the filter-tube to remove all adherent manganese dioxide, and run in 50 cc. acid ferrous sulphate solution. Disintegrate the asbestos fibers with a stirring rod, and after the precipitate is entirely dissolved, titrate with permanganate. The filtering tube is prepared by taking a glass tube thin enough to slide loosely down the stem of a carbon funnel, heating one end until it balls and then pressing out flat. By softening the edge of the flat end and pressing a nail against the circumference at regular intervals the disk can be made fluted. Slip this rod in a carbon funnel, pushing down

until the disk rests solidly, place on it a little dry asbestos, and then pour on it asbestos suspended in water, using a moderate suction to make the pad fairly compact.

ACID FERROUS SULPHATE.

Dissolve 20 grams chemically pure ferrous sulphate in water, add 200 cc. strong sulphuric acid, and dilute to 2 liters.

POTASSIUM PERMANGANATE SOLUTION.

The strength of this solution should be such that 1 cc. equals about 0.0056 gram iron.

STANDARDIZATION AND CALCULATION OF RESULTS.

To standardize both the ferrous sulphate and the permanganate at the same time, take an iron in which the manganese has been accurately determined and treat it according to the method given until the precipitate of manganese dioxide is obtained. Dissolve the precipitate in 50 cc. of ferrous sulphate solution and titrate with permanganate, then run in 50 cc. additional of the ferrous sulphate and titrate again, to obtain the amount of permanganate necessary to oxidize 50 cc. of the ferrous sulphate solution. By deducting the number of cubic centimeters used in the first titration from the number used in the second, we obtain the volume of solution oxidized by the manganese dioxide. Dividing the percentage of manganese in the sample by the figure thus obtained and multiplying this by the number of grams of the original sample, we obtain the value of 1 cc. permanganate in terms of manganese. For instance, if we take 5 grams of a pig iron containing 1.13 per cent. manganese and use 4.6 cc. permanganate in the first titration, and 20.8 cc. in the second titration, then the difference of 16.2 cc. is the measure of the amount of ferrous sulphate oxidized by the manganese dioxide. Dividing 1.13 by this 16.2 and multiplying this by 5 we obtain the value of 1 cc. or 0.0034 gram manganese. The object of standardizing in this way, is to carry out the process under conditions similar to those which occur in a regular determination, for the results obtained by titrating clear ferrous sulphate are always lower than when carbon and asbestos are in the solution, for the reason that the eye of the observer notices the rose tint at once in a transparent solution, but the sharpness of the end reaction is slightly obscured by asbestos and carbon, hence the operator runs

a little past the true point. So that if both titrations are made under like conditions this error is completely eliminated.

The calculations in a determination are made thus: If 5 grams of the sample are taken, 50 cc. ferrous sulphate equals 20.8 cc. permanganate; 1 cc. permanganate equals 0.0034 manganese; 6.2 cc. are required to oxidize the ferrous sulphate not oxidized by the manganese dioxide.

$$\text{Then } \frac{(20.8 - 6.2) \times 0.0034 \times 100}{5} = \text{per cent. manganese.}$$

The time saved by the suspension of the manganese dioxide, and the elimination of silica in the filtering of the manganese dioxide, makes it possible to make a determination in about one hour. The method of standardizing solutions is not based on the reaction that is given in the text-books which is

$\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$, as it was found that solutions standardized on the above reaction were invariably too low in their manganese value. This may be accounted for in the composition of the precipitate, for it is possible that MnO , Mn_2O_3 , Mn_3O_4 , Mn_5O_7 , may be formed in part. At any rate, if we adopt the MnO_2 theory and standardize accordingly, the method will not give the same result on a sample that has the manganese determined by the basic acetate separation and the manganese weighed as manganese pyrophosphate according to Gibbs. On this account it is preferable to use a standardized sample of pig iron.

Below are given some determinations on ores and on some very carefully standardized pig iron.

Results in the first column are by using the Gibbs method.

In the second column by modified Willams method.

In the third by old Williams method, using the MnO_2 theory.

Sample No.	Percentage of manganese.			
	Gibbs method	Modified Willams method	Old Williams method	
Iron ores	1	1.38	1.39	1.11
	2	1.84	1.84	1.51
	3	1.08	1.06	0.91
	4	1.34	1.35	1.20
	5	0.10	0.12	0.08
	6	2.87	2.87	2.14
	7	2.07	2.07	1.83
Pig iron	8	0.415	0.41	0.37
	9	0.442	0.44	0.38
	10	0.97	0.99	0.81

In working on ores carrying large amounts of silica it is advisable to dissolve the sample in hydrochloric acid and evaporate down to dryness, then moisten with hydrochloric acid and heat until the mass softens, and then add a few cubic centimeters of strong nitric acid; evaporate again until chlorine is driven out and then add hot water and filter off the silica and evaporate filtrate and determine manganese as usual.

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ON TRIVALENT CARBON.

(THIRD PAPER).¹

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IT has been shown in the papers published by me on this subject that by the action of metals upon triphenylchloromethane the halogen can be removed quantitatively and that there results an extremely unsaturated hydrocarbon. From the behavior of this substance towards halogens and towards oxygen, the conclusion was drawn that it is an unsaturated radicle, triphenylmethyl. It was shown that the same body results whether carbon disulphide, benzene, ether, or acetic ether is employed as a solvent. It was stated that in the case of the first two mentioned solvents the unsaturated hydrocarbon remains in solution, while with ether or acetic ester as a solvent the hydrocarbon separates in the form of large transparent crystals. This crystalline body possessed all the properties of the unsaturated hydrocarbon, and was also identical with the substance which was obtained when triphenylchloromethane in benzene was acted upon by zinc and the resulting hydrocarbon was precipitated from its concentrated solution by means of ether or acetic ester. Facts have since been discovered which necessitate a modification of this view, and I desire to publish the results even in their present incomplete state.

THE ACTION OF ZINC IN ETHER AS A SOLVENT.

When triphenylchloromethane is dissolved in absolute ether and a strip of zinc is introduced, the solution at once turns yellow and

¹ First paper: This Journal, **22**, 757; Second paper: *Am. Chem. J.*, **25**, 320.