A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF CARBON IN IRON AND STEEL.[1]

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BY dissolving iron in diluted acids or in other solvents employed for this purpose, as cupric sulphate, cupric chloride, mercuric chloride, even free iodine, a part of the carbon escapes as volatile hydrocarbons. The authors affirm that this happens also by heating iron in dry hydrochloric acid gas. Ullgren based his well-known method on the oxidation of carbon by chromic acid and used potassium bichromate and sulphuric acid for the quantitative determination of carbon in iron. But even in presence of such a strong oxidizing agent hydrocarbons escape unoxidized and the method was only made accurate through its modification by Särnström (*Jernkontorets Ann.*, 1884, 385) by conducting the generated gaseous products either over glowing cupric oxide or mixed with air through a narrow, strongly-glowing platinum tube and absorbing the carbon dioxide and determining it by weighing. According to Adolf Tamm (*Jernkontorets Ann.*, 1874, 157) just as accurate a determination of the carbon by weighing as carbon dioxide can be made by burning iron in a current of dry oxygen gas.

The authors have for some time endeavored to complete a new method for dissolving iron, which contains carbon, the solution to be effected in the dry way. After several experiments with melting sodium pyro and metaphosphate or borax, they succeeded in finding a suitable solvent in potassium pyrosulphate, at a temperature at which the purest mercantile potassium bisulphate fuses quietly without giving off gas bubbles. The iron as sheet or drillings dissolves very quickly and completely, the solution getting dark red. Besides carbon dioxide and sulphur dioxide small quantities of hydrocarbons are formed, which even at this high temperature escape unoxidized. The reactions can be expressed in the following equations:

$$2Fe + 12KHSO_4 = Fe_2(SO_4)_3 + 6K_2SO_4 + 6H_2O + 3SO_2.$$

$$C + 4KHSO_4 = 2K_2SO_4 + 2H_2O + CO_2 + 2SO_2.$$

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[1] *Jernkontorets Ann.*, from the *Ztschr. anorg. Chem.*

In this process of fusion there are obtained 1.714 mgms. sulphur dioxide for one mgm. iron and one mgm. carbon gives 10.66 mgms. sulphur dioxide and 3.66 mgms. carbon dioxide. It was the aim of the authors to determine the carbon dioxide in presence of the large quantity of sulphur dioxide with such accuracy that this method could compete with others, *i. e.*, the percentage of carbon has to be determined accurately at least to a unit of the second decimal. This has now been accomplished by the authors by absorbing the sulphur dioxide by chromic acid and the carbon dioxide in a solution of barium hydrate. The barium carbonate formed in this way is then decomposed and the evolved carbon dioxide determined volumetrically. The apparatus necessary to carry out the method is sketched in figures 1 and 5.

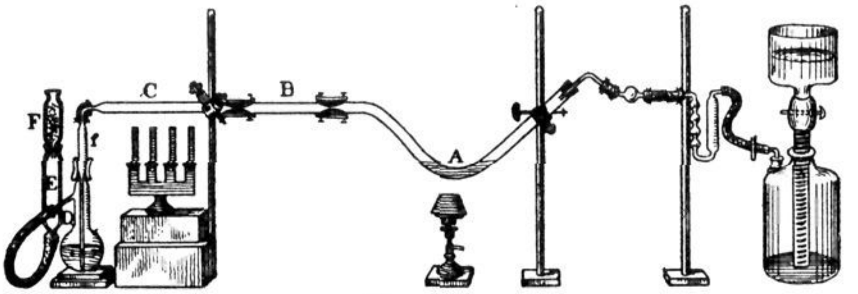


Fig. 1

Fig. 4

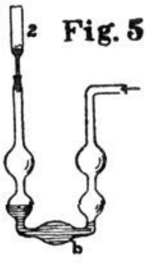
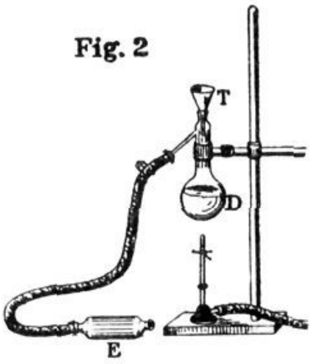


Fig. 5

Fig. 2



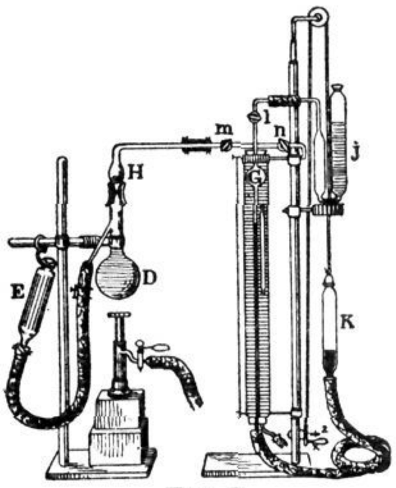


Fig. 3

The solution of the iron is effected in the hard glass tube A, slightly bent, having an interior diameter of fifteen mm.

Thirty-five gms. bisulphate are used for 0.5 gm. iron. The salt is fused for some time in the tube by which operation the particles of dust hanging to the tube and the salt are entirely decomposed. A stream of air free from carbon dioxide is conducted through the tube during the whole operation and while the fusion is cooling, the air is led through continually in large bubbles, so as to form an air canal in the salt. The necessary apparatus—gasometer with water containing sodium hydroxide and two small tubes with baryta water and cotton plugs—are attached to the fusion tube.

After the pyrosulphate is cold, the iron, if it is in the form of sheet, is introduced into the tube without further preparation. Iron drillings, however, have to be weighed and thrown in the tube in a cover of platinum. The apparatus is then filled with air free from carbon dioxide and the pyrosulphate is fused. The gases that are generated are carried off with the current of air and come into contact with the chromic acid crystals in the tube A which especially when they are moist, absorb sulphur dioxide with great rapidity. From there the gases pass into the tube C, where a layer of cupric oxide has been glowing at the moderate heat of a flat burner from the beginning of the experiment, partly to burn the hydrocarbons that are generated and partly to absorb any anhydrides of sulphuric or sulphurous acid, which may have been carried over. As soon as the burner under A has been taken away after the preliminary fusion of the pyrosulphate, the liquid in flask D for the absorption of the carbon dioxide is prepared. This flask, a simple distilling flask the neck of which is drawn out, ought not to have a capacity of more than 100 cc. It is half filled with boiling water, containing three to four drops of hydrochloric acid (all the water used in the experiment contains a little hydrochloric acid) and is allowed to boil (figure 2) to drive out the air completely from the flask and reservoir E. After that, five to six gms. crystallized baryum hydroxide are dissolved in about thirty cc. boiling water, and the liquid which is rendered turbid by barium carbonate is filtered through the funnel T into the flask. In this way there is always a clear solution of baryta in the flask. The funnel without being washed is then taken away, the tube f attached to the neck of the flask D, the burner removed and a protection tube, F, (filled with cotton and potassium hydroxide) is inserted in the reservoir E. The flask is then connected with the tube C as quickly as possible, the connections are made air tight with copper wire, and when the stream of air passes evenly through the apparatus, the fusion of the iron begins. A sheet of 0.5 gm. dissolves in seven minutes; the generation of the gases is rapid and even and ceases instantly when the reaction is finished. The current of air is allowed to pass through the apparatus for ten minutes after the disappearance of the last particle of iron, so as to carry the last trace of generated carbon dioxide into the solution of baryta and to absorb it with certainty.

Professor Petterson has constructed an apparatus for volumetric determination of the carbon dioxide, which gives results as accurate as can be desired. He therefore did not use a method for the determination of the carbon dioxide by weight in the present case, but the above mentioned apparatus. The following operations are necessary to connect the absorption flask D with it: After the carbon dioxide absorption is complete, flask D and tube C are disconnected, and tube f is washed with boiling water and removed. To be sure that there is no sulphur dioxide carried into the solution of baryta by the current of air, it is only necessary to add a couple of small drops of potassium permanganate and shake; if the liquid assumes a rosy color, only carbon dioxide has been absorbed. The flask is then filled with boiled, distilled water up to the narrow side tube, the so-called hydrogen generator (an iron wire, several centimeters long and inserted into a capillary glass tube, for the purpose of preventing the bumping of the liquid when boiling) is introduced, ten cc. hydrochloric acid are put in the reservoir E, D is connected with Petterson's apparatus for the determination of carbon dioxide and the determination completed after his description (*Ber. d. chem. Ges.*, **23**, 1402, *1890*).

From the amount of carbon dioxide obtained by this method a small quantity has to be deducted, which is contained in the reagents, especially in the hydrochloric acid. The correction is found by making several experiments in the apparatus without using iron. The authors mention four of their experiments, which gave 0.246 to 0.249, an average of 0.248 cc. carbon dioxide at 760 mm. and 0° C. The correction therefore is a constant quantity equal to 0.248 cc. Every chemist who uses this method, has of course to ascertain this factor for himself.

In this method 0.10 cc. carbon dioxide equals 0.01 per cent. carbon in the iron. It is easily seen that the small variation of the carbon dioxide in the reagents cannot have any influence on the accuracy of the determination.

The authors give the results of their carbon determinations in some normal irons, which they received through Professor Åkerman from the collection of the Academy of Mines of Stockholm and which come from Miller, Metcalf and Parkin, Pittsburg, Pa. The four samples contained the following quantities of carbon in 100 parts:

	1.	2.	3.	4.
1	1.421	0.817	0.447	0.163
2	1.419	0.810	0.451	0.169
3	1.458	0.817	0.455	0.175
4	1.432	0.813	0.451	0.164
5	1.417	....	0.442	0.169
6	1.431	....	0.444	....
Average	1.430	0.814	0.448	0.168

Whenever iron which contains graphite is analyzed by this method, there is left a residue of fine shining scales of graphite, swimming on the fusion; these can be filtered off after solution of the fusion in hydrochloric acid and taken up by a platinum filter with asbestos (figures 4 and 5). The authors weighed the filter first with the graphite, and then after the burning of the graphite in a current of air loaded with nitrous gases (figure 5) and obtained the weight of the graphitic residue as mentioned in *Ber. d. chem. Ges.*, **23**, 1401, *1890*.

RECENT METHODS IN FERTILIZER ANALYSIS.

EDITED BY EDWIN J. HALEY, A. M.

STOCK'S rapid method for the determination of nitrogen in organic compounds (*Analyst*, **17**, No. 194, 109) has aroused more than passing notice and discussion. Briefly, the original method is as follows: From 0.5–1 gram of substance is mixed in