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## IRONS.

Five independent analyses, made by different individuals, are given for Samples C and D. The methods of analysis used at the Bureau of Standards were, in brief outline, as follows:

*Total carbon.*—Two grams of the iron were dissolved in 100 cc of a solution of copper-potassium chloride containing 300 grams of the salt and 100 cc of concentrated hydrochloric acid per liter. The solution was stirred by a mechanical stirrer. When solution was complete, 5 per cent more of concentrated hydrochloric acid was added and the carbon filtered off on a platinum boat, washed with water and dilute hydrochloric acid, dried at 100°, and burned in a current of oxygen in a porcelain tube, using a ten-burner combustion furnace.

*Graphite.*—Two grams of iron were dissolved in dilute nitric acid (sp. gr. 1.20), using 35 cc and heating very gently. The residue was filtered off on a platinum boat, washed out with hot water, then with a hot solution of potassium hydroxide (sp. gr. 1.10), followed by dilute hydrochloric acid and finally by hot water. After drying at 100°, the graphite was burned in the same manner as the total carbon.

*Combined carbon.*—This was obtained by subtracting graphitic carbon from total carbon.

*Silicon.*—Two grams of iron were dissolved in 30 cc of nitric acid (sp. gr. 1.20) and the solution evaporated to dryness and baked on a hot plate until the ferric nitrate was decomposed. The dish was then cooled and 30 cc of strong hydrochloric acid added to dissolve the ferric oxide. When solution was complete, the acid was evaporated and the residue again baked on the hot plate. Thirty cubic centimeters of strong hydrochloric acid were added and the dish heated until all iron had gone into solution, when hot water was added and the residue filtered off and washed with hot water and dilute hydrochloric acid. The filter and contents were then placed in a platinum crucible and the filter paper and graphite burned off and the residue strongly ignited over the blast. After weighing, the silica was volatilized with hydrofluoric acid with the addition of a little sulphuric acid, and the residue ignited. The difference between the two weights was called silica, and the silicon calculated therefrom.

*Titanium.*—Titanium was determined by treating 5 grams of iron with 40 cc of hydrochloric acid (1 : 1) and heating until all iron had gone into solution. Dissolving in this manner it was found that all but a negligible quantity of titanium remained in the insoluble residue. The filtrate was tested for titanium by extracting the iron with ether after oxidation with a small amount of nitric acid, using the method of Rothe (Stahl und Eisen, 12, 1052 (1892), and 13, 333 (1893),) and adding hydrogen peroxide to the extracted solution, after expelling the ether and oxidizing with nitric acid. In all cases only a faint coloration was obtained. The insoluble residue was filtered off and washed with hot water, and the filter paper and carbonaceous matter were burned. The residue in the crucible was treated with hydrofluoric acid and a little sulphuric acid, and all silicon volatilized.

The residue was fused with sodium carbonate, treated with water, and acidified with sulphuric acid. A sufficient amount of ferric alum was added to the standard titanium solution to give the same tint as the sample when they were at the same dilution, for it was found that the residue from the silica always contained a little iron along with the titanium. Hydrogen peroxide was added to the solution and standard and the comparison made in a Wolff colorimeter.

*Phosphorus.*—Two grams of iron were dissolved in nitric acid (sp. gr. 1.133) and boiled until yellow fumes no longer came off. Ten cubic centimeters of a permanganate solution (15 grams to 1 liter) were added, and the boiling continued. Sodium sulphite solution was added to dissolve the oxide of manganese, and the solution again boiled and filtered. After cooling, 40 cc of ammonia (sp. gr. 0.96) were added, the solution agitated, and when the temperature was at 40°, 40 cc of molybdate solution (prepared according to Blair's "Chemical Analysis of Iron," 6th ed., p. 97) were added and the solution shaken vigorously for five minutes. After settling out, the yellow precipitate was filtered off and washed with acid ammonium sulphate (prepared according to Blair) until the washings did not react for iron or molybdic acid. The precipitate was treated on the filter with 25 cc of ammonia (5 cc of ammonia sp. gr. 0.90 to 20 cc of water). The filter was washed out with water and 10 cc of strong sulphuric acid added to the filtrate, which was then run through the reductor and titrated against a permanganate solution containing about 2 grams to the liter. A blank was always run with the reductor before each titration, using the same quantities of ammonia and sulphuric acid. The insoluble residue was always tested for phosphorus.

*Sulphur, gravimetric.*—Five grams of iron were dissolved in a 400-cc Erlenmeyer flask, using 50 cc of strong nitric acid. A little sodium carbonate was then added, the solution evaporated to dryness, and the residue baked for an hour on the hot plate. The residue was dissolved in 30 cc of strong hydrochloric acid and the solution again evaporated to dryness and baked. Thirty cubic centimeters of strong hydrochloric acid were then added, and, after the iron had dissolved, the solution was evaporated to sirupy consistency and from 2 to 4 cc of strong hydrochloric acid added. When all iron was in solution, between 30 and 40 cc of hot water were added, and the solution was filtered and the residue washed with hot water. The sulphur was precipitated in the cold solution with 10 cc of a 10 per cent solution of barium chloride. The precipitate was filtered off after standing for twenty-four hours. The insoluble residue was ignited, fused with sodium carbonate and nitrate, extracted with water, acidified with hydrochloric acid, evaporated to dryness, extracted with water and a few drops of hydrochloric acid, and the solution precipitated with barium chloride, the sulphur obtained in this way being added to that from the main filtrate. All evaporations were carried on over electrically heated hot plates to avoid sulphur from gas flames, and careful blank determinations were made with all reagents.

*Sulphur evolved as hydrogen sulphide.*—Five grams of iron were dissolved in 60 cc of hydrochloric acid (1 : 1) in the usual evolution apparatus, the air of which had been previously displaced by hydrogen. The hydrogen sulphide evolved was absorbed in a solution of sodium hydroxide (sp. gr. 1.1). The solutions in the absorbing vessels were poured into a beaker and diluted to about 500 cc, acidified with hydrochloric acid, a little potassium iodide added, and titrated with a standard iodine solution, using freshly prepared starch solution as an indicator. Blanks were always made. The iodine solution was standardized against anhydrous sodium thiosulphate (prepared according to Young, J. Am. Chem. Soc., 26, 1028 (1904).)

*Manganese.*—Two grams of iron were dissolved in 30 cc of nitric acid (sp. gr. 1.20), and after filtration the solution was evaporated to about 15 cc. Two grams of potassium

chlorate were added and the boiling continued for fifteen minutes; 10 cc more of strong nitric acid were then added, with 1 gram of potassium chlorate, and the solution boiled ten minutes longer. The precipitated manganese was filtered on asbestos, washed with strong nitric acid till free from iron, and then washed with water till free from acid. The asbestos pad holding the manganese was transferred to a flask and shaken up with 25 cc of a solution of ammonium ferrous sulphate containing 5 per cent sulphuric acid, and when solution of the manganese was completed the excess of ferrous iron was determined by titration with a permanganate solution.

Manganese was also determined as follows: Two grams of iron were dissolved in 30 cc of nitric acid (sp. gr. 1.20). The solution was nearly neutralized with sodium carbonate, and zinc oxide emulsion added. After standing a few minutes, an excess of zinc oxide was added, and the solution made up to a definite volume and one-half or three-fifths filtered off through a dry filter and diluted to about 200 cc. To this were added 20 cc of sodium acetate solution (30 grams crystallized sodium acetate, 30 cc of 30 per cent acetic acid, 170 cc of water) and 40 cc of bromine water. The solution was warmed gently until all manganese had separated. The precipitate was filtered, washed, dissolved, and titrated as before.

*Copper.*—Ten grams of iron were treated with 10 per cent sulphuric acid. All the copper was found in the insoluble residue. This was digested with aqua regia, and excess of ammonia added. The solution was filtered and compared with a standard copper solution treated with the same excess of ammonia.

The methods used by the other analysts were as follows: Booth, Garrett, and Blair used the acetate method for gravimetric phosphorus; Bamber's fusion method for gravimetric sulphur; also an evolution method, absorbing hydrogen sulphide in an alkaline solution of a lead salt, with fusion of the residue; the nitric acid and potassium chlorate separation, with weighing as manganese pyrophosphate, for manganese, and Drown's method for silicon.

Andrew S. McCreath used for silicon both Drown's method and the method of fusion of the residue from the nitric acid solution for phosphorus with sodium carbonate, evaporating the solution of the fusion with hydrochloric acid. He determined sulphur by solution in nitric acid, conversion of this to a chloride solution and precipitation by barium chloride in a small volume. For phosphorus both the acetate and molybdate methods were used, and for manganese the chlorate method.

Cremer and Bicknell used the molybdate separation for phosphorus, weighing as pyrophosphate; oxidation with nitrohydrochloric acid and precipitation in the ferric chloride solution for sulphur, and the acetate separation and weighing as  $Mn_2O_4$  for manganese.

Albert W. Smith used the molybdate separation for phosphorus, weighing as magnesium pyrophosphate; oxidation with nitrohydrochloric acid and precipitation in the ferric chloride solution for sulphur; the acetate separation and weighing as manganese pyrophosphate for manganese, and Drown's method for silicon.

In all cases the total carbon was determined by solution in copper-potassium chloride solution and combustion of the residue, and the graphite by solution in dilute acid and combustion.

#### STEELS.

The methods used by the Bureau of Standards were as follows:

*Carbon.*—Besides the solution and combustion method outlined above, carbon was also determined by direct combustion in oxygen in a Gooch tubulated crucible. (See Blair, 6th ed., p. 139.) In the more recent samples, results by this method only are reported.

*Silicon*.—In the recently prepared samples silicon was determined by Drown's method and by the method above described under "Iron." Usually the residue from the oxidation sulphur determination was used for this latter method.

*Phosphorus*.—Determined as described under "Iron," omitting usually the filtration after solution of the metal.

*Sulphur*.—Method same as for iron.

*Manganese*.—Determined as in iron.

In all the later certificates of analyses the methods used by the other analysts are indicated on the certificate.

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Approved:

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