considered the section where crystals could yet be found in the amorphous mass.

As an average may be taken for the formation point of carborundum 1950° C. and as its decomposition point into graphite and silicon 2220° C.

ELECTROCHEMICAL LABORATORY, COLUMBIA UNIVERSITY,
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VOLUMETRIC METHOD FOR THE ESTIMATION OF CARBON IN IRON AND STEEL WITH THE USE OF BARIUM HYDROXIDE.[1]

BY JAMES A. AUPPERLE.

Received May 16, 1906.

THE method which I am about to describe has been found to compare very favorably with results obtained by gravimetric methods, with the advantage of being more rapid. It is based upon the following data:

First.—Barium hydroxide can be titrated with acids in the presence of barium carbonate (which is neutral or faintly alkaline to phenolphthalein), and no carbonic acid will be lost.

Second.—Carbonic acid is indicated by phenolphthalein, and when any barium carbonate is dissolved by standard acid during titration, the fact will be shown by the change in color.

Third.—Barium hydroxide can be titrated with acids without filtering off the barium carbonate, providing the acid is run into the mixture by a prolongation of capillary tube attached to the burette and extending well into the solution that is being titrated.

The reason for using the capillary tube is that if any carbonic acid be liberated in the lower portion of the beaker, it would be reabsorbed by the upper portion containing barium hydroxide.

Hydrochloric acid has been found to give the best results, and an acid a trifle less than N/5 is used. This is prepared by mixing 15 cc. of acid (1.20) and 1000 cc. of water. One cc. will approximately equal 0.001 gram carbon.

The barium hydroxide solution is prepared from 31.5 grams of Merck's crystallized salt ($Ba(OH)_2,8H_2O$) dissolved in 1000 cc. of boiled water. When both acid and alkali are at room temperature, and without waiting for the suspended barium carbonate to settle completely, a measured portion is titrated with acid, and the remaining barium hydroxide is then diluted with water,

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[1] Read before the Indiana Section of the American Chemical Society at Lafayette, Ind., May 12, 1906.

so that 1 cc. = 1 cc. of acid. The barium hydroxide is then allowed to stand until clear, and again titrated with acid.

The phenolphthalein solution is 1 to 30 of alcohol, and as it usually contains acid, it is rendered pink with dilute caustic soda or potash. Three drops of phenolphthalein are used for each titration.

When sulphuric or oxalic acid is used for titrating, the barium sulphate or oxalate formed in addition to the barium carbonate present, renders them less desirable than hydrochloric acid, which forms no precipitate.

In using this method in connection with burning steel filings in a current of oxygen, an accurate determination of carbon can be made in twenty minutes, which includes the time consumed in filing the steel.

I have found that filings carefully taken, check well in carbon, as found in borings secured in the usual manner, with the advantage that an ignition can be made at a lower temperature and in less time.

The following table will show how the time is distributed in making a direct combustion.

	Minutes.
Filing the sample	4
Weighing sample and placing dish in Aupperle combustion crucible	2
Measuring barium hydroxide, attaching Meyer tube to combustion apparatus, starting oxygen and lighting gas	3
Ignition of borings	8
Emptying, washing bulb and titrating	3
	20

In filing the sample, a large file which has been previously cleaned with a stiff brush is used. The filings are weighed and placed in a platinum dish that fits the Aupperle crucible. This dish contains a $^{1}/_{8}$ inch layer of 120 mesh emery which is heavier than the precipitated alumina ordinarily used and is not so easily projected out of the dish.

The platinum dish is covered with a disk of platinum foil perforated in two semi-circles which form wings, one bent into and the other out of the dish. The wings are bent at angles of 45° which prevent anything being projected out of the dish.

I have found that with two ounces of gas pressure and gas averaging 700 B. T. U. per cubic foot the crucible becomes white hot, and steel filings are completely oxidized in eight minutes. A Bunsen vertical blast-lamp gives good satisfaction.

At least twenty pounds of air pressure should be used. A single cylinder compressor making 150 revolutions per minute gives enough air for two lamps. By simply closing the valve through which the air enters the pump, a five-pound vacuum can be maintained and used for suction filtering.

Mr. Philo Kemery, of the Crescent Steel Works, Pittsburg, devised the spiral educt tube of the Aupperle crucible which I have adopted and found very satisfactory. The present form of the crucible has one coil of the educt tube around the crucible and joined to the side instead of the bottom. This permits more heat to be concentrated on the bottom of the crucible, and the educt tube becomes hot enough to oxidize all carbon to carbon dioxide.

The standard barium hydroxide and standard acid are contained in bottles holding twelve liters, each bottle being supplied with compressed air in order to facilitate rapid measuring.

The air that enters the barium hydroxide bottle is passed through a solution of caustic potash.

The capillary tube attached to the burette stop-cock is about five inches long.

For carbon determinations in steel 75 cc. of barium hydroxide are used, but for iron 150 cc. contained in two Meyer tubes should be used, each containing 75 cc. The second tube will only show a precipitate of barium carbonate when a very rapid current of oxygen gas is used, or when the sample is extremely high in carbon. Iron borings should be ignited for twelve to fifteen minutes, and the oxide of iron remaining in the dish should be fused into one globule. The original shape of the borings should then have entirely disappeared.

The barium hydroxide and carbonate are poured into a beaker, and the Meyer tube rinsed three times with boiled distilled water. Three drops of phenolphthalein indicator are added and standard acid run in very rapidly until the red color disappears and the white barium carbonate is seen. The beaker is then removed and placed under a burette containing standard barium hydroxide, which is added slowly, and until the original red color returns. The number of cubic centimeters barium hydroxide used in titrating back is subtracted from the acid burette reading. Only about 1 cc. is usually required.

In experimenting to find how much carbon dioxide would be lost by adding sufficient standard acid to dissolve all the barium carbonate, and immediately titrating back with barium hydroxide, 75 cc. of acid were added to the mixture of barium hydroxide and carbonate from a 0.90 per cent. carbon steel, and on titrating back to original pink 0.88 per cent. was found, thus showing practically no loss of carbon dioxide even when all barium carbonate is dissolved.

The acid is standardized with steel or iron of known carbon content. For steel the theoretical value may be used, 1 cc. N/5 acid =0.0012 gram carbon. The following table shows how well the method checks with the gravimetric methods.

	Weighing as $BaCO_3$. Gravimetric. 3-Gram samples.	Volumetric. 3-Gram samples.
Steel standard	0.090	0.090
" "	0.115	0.113
" "	0.380	0.393
" "	0.643	0.627
" "	0.735	0.725
	1-Gram samples.	1-Gram samples.
" "	0.890	0.890
" "	1.130	1.150
" "	1.350	1.330
Iron	2.89	2.93
"	3.30	3.35
International standard	3.25	3.31
" "	3.67	3.65
Iron	3.76	3.72
"	4.30	4.32

The following results are reported by Mr. J. C. Dickson of the Inland Steel Co., Indiana Harbor, Ind., to whom I extend thanks for investigating this volumetric method.

	Gravimetric method by KOH.	Volumetric.
Steel	0.463	0.460
"	0.890	0.896
"	0.934	0.929
"	1.097	1.101

To show that practically no barium carbonate dissolves during titration, several samples, after being titrated, were filtered and the barium carbonate weighed with the following results:

	Volumetric method.	Gravimetric after titration.
Carbon	0.89	0.88
	0.97	0.97
	2.73	2.75
	2.75	2.80
	3.17	3.20
	3.58	3.59
	3.84	3.83

Many chemists prefer burning the carbonaceous residue, and I have found that graphite is rapidly oxidized if filtered on a small Gooch crucible and then without drying or removing the asbestos, the Gooch is immediately placed *bottom up* in the combustion crucible. Fifteen minutes burning will be ample time using about 60 cc. oxygen gas per minute.

I wish to avail myself of this opportunity to thank Mr. H. A. Schwartz, the Secretary of the Indiana Section of the American Chemical Society, for investigating synthetic mixtures of various amounts of dried, and also freshly precipitated barium carbonate, when mixed with various amounts of standard barium hydroxide and titrated with acid.

The Aupperle crucible is described in *Iron Age* of October 6, 1904; abstracted in *Iron and Steel Magazine*, December, 1904.

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THE DETERMINATION OF CARBON IN IRON AND STEEL BY DIRECT IGNITION WITH RED LEAD.[1]

BY CHARLES MORRIS JOHNSON.

Received January 22, 1906.

THE writer's experience with this method for the determination of carbon, together with some notes on what led to its adoption for routine combustion analysis, may prove of interest.

The solution of steel drillings containing large percentages of chromium, tungsten or molybdenum in double chloride of copper and potassium causes more or less loss of carbon as hydrocarbon. Especially sensitive to such loss are the carbides that are separated by the double chloride from steels in which are 10 or 12 per cent. of molybdenum together with several per cent. of chromium.

These carbides may lose some of the carbon by contact with

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[1] A preliminary paper was read at the December meeting of the Pittsburg Section of the American Chemical Society.