that of water that the measure may be accepted as cubic centimeter for gram.

DETERMINATION OF ACETONE IN THE PRESENCE OF ETHYL ALCOHOL.

The standard dilution of acetone containing ten grams in the liter was used, and ten cc. of this required 14.3 cc. of the hypochlorite solution.   On repetition 14.4 cc. was required.

A dilution of ethyl alcohol was made containing ten grams in the liter, and ten cc. of this requires one-tenth cc. of the hypochlorite.   On repetition 0.125 cc. was required.

To ten cc. of the acetone dilution two-tenths cc. of the alcohol dilution was added, and this mixture required 14.4 cc. of the hypochlorite solution.   On repetition 14.4 cc. again was required.

To ten cc. of the alcohol dilution two-tenths cc. of the acetone dilution was added, and this mixture required 0.35 cc. of the hypochlorite.   On repetition four-tenths cc. was required.

In each case ten cc. of the iodine and soda solution was used and all other conditions were kept fairly uniform.

In the case wherein the hypochlorite was added to alcohol alone no precipitate nor cloudiness was visible, although 0.1 to 0.125 cc. was required to obtain the starch reaction.   When acetone had been added to the alcohol one-half this quantity of the hypochlorite was sufficient to give decided cloudiness.

These results appear to confirm the conclusions of Robineau and Rollin to the effect that the presence of ethyl alcohol has no effect upon the titration of acetone by this method, although ethyl alcohol is an iodoform-yielding substance.   The small quantity of hypochlorite required to obtain the starch reaction when alcohol alone was titrated was probably in consequence of traces of impurity in the alcohol.

THE DETERMINATION OF SULPHUR IN CAST IRON.

BY FRANCIS C. PHILLIPS.

IN a paper read before the American Chemical Society in August, 1895,[1] I have detailed some experiments made in the determination of sulphur in white cast iron by the evolution method, and have attempted to show that the loss of sulphur in its

[1] This Journal, 17, 891.

determination in such iron may be due to the formation of organic sulphur compounds not oxidizable to sulphuric acid by the usual means.

By passing the gases evolved during the solution of the iron in hydrochloric acid through a heated porcelain tube it was found that the volatile organic sulphur compounds may be decomposed and nearly all the sulphur recovered by conversion into hydrogen sulphide, oxidation and precipitation as barium sulphate.

In judging of the correctness of an analytical method it has been necessary in the case of the majority of the constituents of iron to depend upon a single criterion; that method is regarded as most accurate which, being correct in its details, yields the highest percentage of the constituent sought to be determined. For it is hardly possible to add to pure iron a known percentage of sulphur, phosphorus or carbon, and test the method by a determination of the added constituent.   For the determination of sulphur in iron it has been common to regard the method of oxidation and solution of the iron by nitric acid, followed by precipitation of the sulphur in form of barium sulphate as the most accurate, inasmuch that it yields results somewhat higher than those obtained by other modes of procedure.

It does not seem probable that an appreciable error could occur in the use of this method unless, in the simultaneous oxidation of the carbon and sulphur of the iron, an organic sulphur compound should be formed.

It has seemed to be of interest, however, to apply a method for the determination of sulphur by which all the constituents of the metal could be completely oxidized in a dry state and at a high temperature, in order to avoid as effectually as possible the chances of loss due to the conversion of sulphur into a volatile compound not oxidizable by ordinary means to sulphuric acid.

In searching for a method which should answer these requirements, it seemed possible that by heating the iron in the form of fine powder in presence of a mixture of alkaline carbonate and nitrate the sulphur might be oxidized directly and completely to the condition of a sulphate without affording an opportunity

for the escape of a trace of sulphur in some intermediate volatile or soluble compound. Accordingly an experiment was tried in the following way :

An iron containing its carbon in the combined form was melted in a crucible and poured while fused into water. The granulated metal was crushed in a steel mortar to an extremely fine powder. The powder so obtained was sifted through bolt-ing sheeting.

Two and one-half grams of the sifted iron were mixed with ten grams of a mixture of equal parts of sodium nitrate and car-bonate in a platinum crucible. The crucible was covered and heated over a Bunsen burner. At a red heat a sudden and rather violent reaction occurred, and having been begun, was easily maintained with very little aid from the burner flame. The reaction appeared to be complete in a few minutes. After heating for a half hour the crucible was cooled and its contents softened in water. A residue of a reddish brown powder, con-sisting of ferric oxide with a little ferrous oxide, was obtained. This residue was found to contain no sulphuric acid, and on digesting with hydrochloric acid dissolved without effervescence, showing that none of the particles of the original iron had remained unoxidized. From the results of this experiment and others which need not be detailed here, it seemed to be possible to oxidize finely divided iron so completely by heating with sodium carbonate and nitrate, that its sulphur might be con-verted quantitatively into sulphuric acid.

The mixture of sodium carbonate and nitrate although tend-ing to oxidize finely divided iron seems to exert a less powerful action upon the carbon contained in the iron, and this carbon may appear as a black residue after the fused mass has been softened and extracted by water and the ferric oxide dissolved in hydrochloric acid.

It seems to be important for the success of the method that in the oxidation of the iron the carbon should also be nearly or completely oxidized, for if the carbon remained unburned a por-tion of the sulphur might escape oxidation. In general it may be said that the order of oxidation of these three elements by the method used is as follows : 1, iron ; 2, carbon ; 3, sulphur ; the

iron being the most easily oxidized, and the sulphur the most difficult to oxidize. This order is not exactly what we should anticipate, but it is to be remembered that unless the iron grains are fine enough to be penetrated by oxygen, and changed completely into a soft powder of ferric oxide, the sulphur and carbon have no opportunity to oxidize at all. If the iron could be used as an impalpable powder the order of oxidation would probably be different. The marked resistance of the carbon to oxidation has been frequently observed, even when using more sodium nitrate in the fusion than is theoretically enough to completely oxidize both iron and carbon, supposing that the sodium nitrate is reduced only to nitrite in the process.

Experiments of a similar kind were tried with ferromanganese. A metal containing about eighty per cent. of manganese was used. By crushing in a steel mortar this iron was very easily reduced to a powder fine enough to pass through bolting sheeting. On heating the powder with the mixture of sodium nitrate and carbonate a most violent reaction occurred, the metal burning with a long flame, extending several inches above the crucible. In order to control the reaction it was found necessary to melt one-half of the fusion mixture to be used in the crucible and then add slowly the other half, previously mixed with the powdered metal, while stirring constantly. In this way the reaction could be easily controlled. On softening the fused mass in water it was found that the iron had been peroxidized and the manganese changed to binoxide. No trace of sodium manganate was ever formed, the solution in water being after filtration invariably colorless. No carbon was found in the residue. The oxidation of the carbon is much more easily effected in the case of iron containing a high percentage of manganese. In all the trials made the silicon of the iron was oxidized, but it was found that when the fused mass is softened in water very little silica enters into solution as an alkaline silicate, the greater portion remaining insoluble and in a flocculent form.

Experiments were then tried with a gray iron. This form of iron could not be crushed to a fine powder, and an experiment was made in reducing it from small drillings by means of a

chilled iron rubber and plate, such as is ordinarily used for grinding ores. Several gray irons were tried in this way. Some could not be powdered by the method just mentioned, the grains tending to flatten instead of being crushed. Others were readily reduced, but the powder was not in any case fine enough for sifting through bolting sheeting. It was found in the case of a gray iron reduced to powder by the method of grinding, that on fusion with the mixture of sodium nitrate and carbonate, used in the preceding experiments, the graphitic carbon of this iron was more readily burnt than the combined carbon of white iron.

As it had proved to be a somewhat difficult matter to oxidize completely the carbon of the iron in the various experiments made with the fusion method, notably in the case of white iron, some trials were made in the use of sodium peroxide. This proved to be a more efficient oxidizing agent for iron and its contained carbon than sodium nitrate. For these trials a mixture was used consisting of forty-five parts each of sodium peroxide and sodium nitrate, together with ten parts of sodium carbonate.

White iron was oxidized and its carbon burnt during a fusion lasting less than ten minutes.

On heating ferromanganese with this mixture the iron was found to be completely oxidized. The carbon was burnt and the manganese was oxidized and converted into sodium manganate, yielding a deep green solution when the fused mass was digested in water.

An admixture of sodium carbonate to sodium peroxide tends in all cases to diminish its action upon finely divided iron at a high temperature and renders the process more easily controlled. It seemed to be possible to base a method for the quantitative determination of sulphur in certain kinds of cast iron upon the reactions described above.

An indispensable condition of success in the use of the method is found in the extreme fineness of the iron. In the case of white irons the fineness of the powder has been secured by

crushing in a steel mortar until the powder passed through a sieve of bolting sheeting or bolting cloth.[1]

Some gray irons cannot be crushed or ground. To these the method is not applicable. For gray irons, however, the evolution method answers all requirements.

The following details are given of the method finally employed :

1. *White iron.*—About one and one-half grams of the finely powdered and sifted metal was intimately mixed with eight grams of the sodium peroxide mixture above mentioned, or with four grams each of sodium carbonate and nitrate. The somewhat violent reaction set up on the application of strong heat to the platinum crucible was completed in a few minutes. The crucible was heated for about twenty minutes in all. After cooling the contents were softened in water, the solution decanted and the residue ground, while wet, in a mortar. The solution and residue were then digested in a beaker on the water-bath for one hour after addition of two cc. of strong bromine water. The liquid was then filtered, acidulated with hydrochloric acid, evaporated to dryness to separate the small portion of silica which had entered in solution and filtered. The sulphuric acid was determined in the filtrate in the usual manner. The barium sulphate obtained was always white. If the fusion mixture contains sodium carbonate and nitrate, but no sodium peroxide, the crucible must be heated for a longer time, but a portion of the carbon of the iron may still remain unoxidized.

2. *Ferromanganese.*—In this case it is better to use a mixture of equal parts of sodium nitrate and carbonate, omitting the sodium peroxide.

Ten grams of the mixture were divided into two portions, one of which was fused in a crucible. The other portion mixed with two or two and one-half grams of the finely powdered iron

[1] Two different materials are sold which are suitable for the sifting. One is called bolting cloth, the other bolting sheeting. The bolting cloth used in these experiments contained about eighty-five meshes to the linear inch, while in the bolting sheeting about one hundred and thirty-five were counted. The material having the smaller number of meshes is made of coarser threads, however, and yields, on account of the smaller openings, a finer powder. Bolting cloth is, on this account, better suited to the preparation of a sample of white iron for a determination of sulphur by the method described.

was then slowly added.   Although too violent combustion of the iron is to be avoided, it seems to be important, for the success of the method, that a reaction of decided intensity should occur during the fusion.

Sodium nitrate possesses an advantage over sodium peroxide in its greater purity, the former compound being readily obtainable with practically insignificant traces of sulphur.

Natural gas was the fuel used for the Bunsen burner in heating the charges.   This gas was found by repeated experiments, not to contain a sufficient quantity of sulphur to affect the purity of the sodium carbonate when heated in a platinum crucible in the same manner as in the case of the determinations described.

The usual occurrence of sulphur compounds in coal gas would preclude its use in the application of the method.

From the experiments, the results of which are stated in the accompanying table, there seems to be some reason to suppose that not quite all the sulphur of the iron is converted into barium sulphate when the metal is oxidized and dissolved by nitric acid. That it has been completely recovered by the process of fusion cannot be positively asserted.[1]

The method I have described is not proposed as a substitute for any existing method.   The purpose of the present work was merely to ascertain as far as possible whether by a process of direct oxidation of the iron in a dry state a larger proportion of the sulphur could be recovered in weighable form than by the usual method of oxidation and solution in nitric acid.

My thanks are especially due to Mr. F. B. Smith for great care and attention to detail in conducting the experiments I have detailed.

[1] The method of preparation of a sample for analysis in the case of the more brittle forms of iron, by crushing in a steel mortar and sifting, is suggested in Regnault's Elements of Chemistry, translated from the French by Betton, 1867, **2**, 112.

Character of iron used.	Fusion mixture employed.	Percentage of sulphur found by fusion.	Percentage of sulphur found by the method of oxidation by nitric acid.
White iron A crushed in mortar and sifted through b o l t i n g sheeting.	Contained equal parts of sodium carbonate and nitrate.	0.112	0.101
		0.112	0.098
		0.111	0.096
		0.107	0.099
		0.114	0.100
		0.114	0.102
		0.106	0.102
		0.108	0.104
		0.107	
		0.103	
Means		0.109	0.100
White iron B crushed and sifted.	Contained 45 parts $NaNO_3$ 45 parts Na_2O_3 10 parts Na_2CO_3	0.155	0.143
		0.150	0.149
		0.130	0.143
		0.139	0.147
		0.166	
		0.156	
		0.156	
		0.161	
		0.151	
Means		0.151	0.145
F e r r o m a n g a n e s e crushed and sifted.	Contained equal parts of sodium nitrate and carbonate.	0.022	0.012
		0.027	0.013
		0.018	0.012
		0.018	0.010
		0.018	
		0.019	
		0.016	
Means		0.020	0.012
Gray iron drillings powdered by rubber and plate. Not sifted.	Contained equal parts of sodium nitrate and carbonate.	0.034	0.027
		0.030	0.030
		0.036	0.026
		0.034	0.028
		0.033	0.028
		0.034	0.022
Means		0.033	0.027