

# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

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## SOME PRESENT POSSIBILITIES IN THE ANALYSIS OF IRON AND STEEL.<sup>1</sup>

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To the analytical chemist, there are few substances in nature, more interesting than a piece of pig iron, few substances which have received more study, and few which present chemical problems more difficult of solution. The amount of work which has already been done in connection with this very common but very complex substance, is something enormous. Indeed, if we add to the study which has already been put on pig iron itself, the work which has been done on what may perhaps fairly be called its progenitors, *viz.*, the ores, the fuel, the flux, and the refractory materials used in its production, and then consider still farther the labor already expended in the analysis of what we may call the progeny of pig iron, *viz.*, castings, wrought iron, malleable iron, and the numerous grades and kinds of steel, made by the various processes of the present day, we shall surely be safe in saying that more chemical work has been done in connection with pig iron, than with any other substance in nature. Is it too much to affirm that at the present time one-third, possibly one-half of all the chemical work done in the world, is in connection with the iron industry, either in the solution of unworked-out problems, the development of new methods of analysis, or in the routine analyses affecting the interests of producer and consumer.

But the amount of work already done and in daily progress in connection with this substance, is not all that may be said in

<sup>1</sup> Presidential address delivered at the Troy meeting of the American Chemical Society, December 29, 1896.

regard to it. The complexity of pig iron is very great, and consequently the analytical problems presented are far from being easy of solution. It may not be uninteresting to enumerate some of the substances which have already been found in pig iron. We find, besides the element iron, carbon, phosphorus, silicon, sulphur, manganese, copper, chromium, tungsten, titanium, vanadium, nickel, cobalt, aluminum, potassium, sodium, magnesium, calcium, and lithium. It is fair to say that there is apparently well grounded belief that the last five are characteristic of intermingled slag, rather than of the metal itself. It is not intended that it should be understood that all of these substances have been found in any one sample of pig iron, but that all these substances have actually been detected in the analysis of this alloy. Indeed there seems no reason why any element, which either occurs in the metallic condition in nature, or which is reducible to that condition by carbon, and which is not volatile at the temperature of the blast furnace, may not occur in pig iron, provided of course it will alloy with the metal. Quite a large number of other substances besides those mentioned above have actually been alloyed with some form of iron or steel. Among these may be mentioned zinc, tin, lead, antimony, bismuth, molybdenum, silver, platinum, rhodium, iridium, palladium, and gold. Nor is this all that may confront the analyst, who devotes himself to the chemistry of iron and steel. Not less than three elements which usually exist in nature in the gaseous form, occur in these metals, and are believed to have important influences on their physical properties. These are oxygen, hydrogen, and nitrogen; while the numerous analyses show the presence of carbon monoxide in both cast iron, wrought iron, and steel. It seems quite evident that the chemist who hopes to successfully cope with the problems which are involved in even the ultimate analysis of iron and steel in their various forms, must be well equipped with a liberal share of the methods and processes known to mineral chemistry, and on the other hand, if he attempt the proximate analysis of these substances, or the separation and determination of the various compounds of the elements present, with iron or with each other, he will at least be brought on the border ground of organic chemistry. Some of the carbon compounds

which are characteristic of the brilliant work of the present president of the French Chemical Society, are known to occur in or have already been isolated from pig iron.

It would lead us too far from our present purpose to do anything more than enumerate the largest number of the elements given above. Suffice it is to say that in what follows, we shall confine ourselves to the five first mentioned; *viz.*, carbon, phosphorus, silicon, sulphur, and manganese. And the question which we shall ask ourselves is, 'What is the present condition of a portion of the analytical methods for the determination of these substances, considering these methods both in regard to their accuracy and speed?' One word of precaution. It would be manifestly impossible to comment on all the methods in use for determining these constituents. To enumerate them alone would weary your patience. We shall confine ourselves, therefore, principally to methods which may be or are used when the diverse interests of producer and consumer are involved.

Beginning then with total carbon in pig iron, wrought iron, and steel, we deem it safe to say that the method by combustion in oxygen gas, as at present known and worked in many laboratories, leaves very little to be desired, so far as accuracy is concerned, and is sufficiently rapid for most commercial uses. The modification introduced some years ago, of using a solution of the double chloride of copper and ammonium, instead of simple chloride of copper,<sup>1</sup> to release the carbon from the iron, took away from the combustion method, one of its greatest difficulties; *viz.*, the long time required to dissolve the metal. This modification, as many will doubtless remember, reduced the time required for solution, from two or three days, to an hour or less. Indeed, at the present time, if a good stirring machine is used, it is quite possible to dissolve three grams of fairly fine borings of pig iron, wrought iron, or steel, in 200 cc. of the proper solvent in from ten to forty minutes. Still further the studies of the Committee on International Standards for the

<sup>1</sup> It is difficult to say positively who first suggested this modification. The first mention in literature that we are able to find is in the *Transactions of the American Institute of Mining Engineers*, 4, 157, by J. B. Pearse. But a private communication from Andrew S. McCreath, states that he made the suggestion while working under Pearse, and that Professor Richter, in the *Leoben Jahrbuch*, had previously suggested the use of potassium or sodium chloride with copper chloride, which led him to try the ammonium salt. McCreath's description of the method as used by himself, is published in the *Transactions of the American Institute of Mining Engineers*, 5, 575.

Analysis of Iron and Steel, have further modified the method, and it is believed rendered it much more accurate. Among these modifications may be mentioned the use of an acid instead of a neutral or basic solution of the double salt to dissolve the metal. This point was thoroughly worked out by Blair.<sup>1</sup> Following this came the work done in the laboratory of the Pennsylvania Railroad Company,<sup>1</sup> demonstrating the unreliability of the use of the double chloride of copper and ammonium as a solvent, owing, as appeared later, to the probable presence in all ammonia and its salts, obtainable in the market, even those marked "C. P.," of some carbonaceous material, possibly pyridine,<sup>2</sup> derived from the gas liquor used in making the ammonia. The substitution of the potassium,<sup>2</sup> for the ammonium salt, has apparently completely overcome this difficulty, and this with the use of oxygen gas instead of lead chromate, in which to burn the carbon, and some modifications of the absorbing and purifying train,<sup>3</sup> have seemingly placed the dry combustion method for determining carbon in the front rank of successful and accurate analytical processes. The principal known source of error in the method at the present time appears to be in connection with the weighing. The potash bulbs and small calcium chloride tube used in absorbing the carbon dioxide weigh, altogether, some fifty to sixty grams, and present considerable surface. If now, between the weighing before the combustion and the weighing after the combustion, the interval being an hour, or a little more, there is considerable change in the hygroscopic condition of the atmosphere, an error of 0.01 percent. may be easily introduced. If we may trust our experience, it is difficult to make closely agreeing duplicate combustions in showery weather. Blair suggests a method of overcoming this difficulty consisting in having a second potash bulb and calcium chloride tube of, as nearly as possible, the same size on the opposite end of the balance when weighing.

In regard to the accuracy of the method as at present understood, it may be said, that undoubtedly the best test of the accuracy of a method, is the recovery of a known amount of any substance added to the material to be analyzed. This proce-

<sup>1</sup> *Trans. Am. Inst. Mining Eng.*, 19, 614.

<sup>2</sup> *Trans. Am. Inst. Mining Eng.*, 20, 242.

<sup>3</sup> *This Journal*, 15, 448.

ture being manifestly impossible in the case of iron and steel, we are compelled to judge of the accuracy of the combustion method, as applied to these metals, in some other way. For this purpose, however, we have at hand the results obtained by different chemists, using different methods, but working on the same samples. In the course of the work done by the Committee on International Standards for the Analysis of Iron and Steel, the carbon in four samples of steel was determined, First, by using acid double chloride of copper and potassium as solvent and burning in oxygen gas; Second, by using the same solvent and burning in chromic acid solution; and Third, by treating the borings direct with bisulphate of potash and heat, conducting the carbon monoxide and sulphur dioxide formed over hot solid chromic acid, which oxidized both gases and retained the sulphur trioxide formed, and finally measuring the volumes of the resulting carbon dioxide in an eudiometer tube. Each method was used by a different chemist. The results obtained are as follows, the letters at the side representing the four samples of steel, the figures at the top representing the chemists, and the figures in the columns the percentages of carbon in the steel samples :

	1.	2.	3.
A.....	1.455 <sup>1</sup>	1.440 <sup>1</sup>	1.450 <sup>2</sup>
B.....	0.815	0.800	0.815
C.....	0.450	0.450	0.448
D.....	0.152	0.185	0.168

The agreement of the results on the first three samples is quite marked. The discrepancy on the fourth sample has not been explained. The matter is discussed in considerable detail in reference 1, but we think it safe to conclude that so far as method goes, the determination of total carbon in pig or cast iron, wrought iron and steel, is reasonably accurate.

The speed of the combustion method as at present worked in good laboratories is quite remarkable, compared with the possibilities twenty-five years ago. A sufficient supply of sample borings being at hand, one operator using two furnaces, may readily make from fourteen to sixteen combustions in a day of eight hours, it being understood that the bulbs are weighed with

<sup>1</sup> *Proc. Eng. of Western Penna.*, 9, [9], 35.

<sup>2</sup> *Ztschr. anorg. Chem.*, 4, [3] und [4], 505.

oxygen gas in them instead of air, and that the last weight of each combustion, except the last one at night, is taken as the first weight of the succeeding one. It is, of course, assumed that when turning out the amount of work above described, the furnaces and apparatus are all in good order, and everything working well. Accidents, an occasional overhauling of the apparatus, blank combustions from time to time for testing purposes, and once in a while an obstinate steel that refuses to dissolve in time or gives trouble in filtration, will all tend to diminish output. The results obtained with this rapid work show, when duplicates are made, occasional discrepancies as high as three hundredths of a per cent. in a steel containing one per cent. of carbon, but we have seen very large numbers of duplicates, made as above described, which did not disagree one one-hundredth.

Again, when work is not so plentiful as to admit of the procedure described above, the method still permits satisfactory speed. Starting with a fresh sample of borings and everything in good order, but cold, it is not difficult to get two closely agreeing determinations on the same sample in two hours and a half. Of course, in investigation or referee work, more time would undoubtedly be used, especially if the interests involved are very great. But we have many times been astonished in our own laboratory, at the close agreement between the results obtained in the rapid manner described above, and the duplicate analysis made on the same sample for confirmatory purposes, but using much more time and pains.

Turning now to the determination of combined carbon and graphite, we do not find the state of affairs so satisfactory. As is well known, these two constituents are usually found by first determining total carbon, then dissolving another portion of the sample in hydrochloric acid, filtering and washing with caustic potash, alcohol, and ether, and then burning the residue, collecting and weighing the carbon dioxide formed, as in an ordinary combustion. The result is called graphite, and the combined carbon is the difference between the total carbon, and the graphite. But as Shimer<sup>1</sup> has so well shown, what we actually get by this procedure is not necessarily the graphite and the

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 25, 395.

total combined carbon in the sample, but only the combined carbon which exists in the metal as a carbide soluble in hydrochloric acid. If the sample contains carbides not soluble in that acid, nor in the materials used in washing, the carbon of these carbides appears with and is counted as graphite. Shimer shows that titanium, and possibly vanadium carbide, are apparently not infrequently thus counted. The use of sulphuric instead of hydrochloric acid leads to the same error, while the employment of nitric acid as solvent, apparently gives the graphite much more definitely, but leaves us in doubt as to whether the combined carbon is really the combined carbon which we want, in order to have light on the quality of the metal we are dealing with. It is obvious that the difficulty here is in our lack of knowledge as to what carbides actually exist in pig and cast iron, and if there are several of them, which one or ones do we actually want to know the carbon content of. If we knew positively that the combined carbon wanted was that which exists in the metal as carbides of iron and manganese, and that these carbides were soluble in hydrochloric or sulphuric acid, while all other carbides present were not soluble in these acids, obviously we should use these acids when determining combined carbon. On the other hand, if we want to know only graphite, and care little about the combined carbon, apparently nitric acid is the solvent to use. It is clear that much more work is needed on this subject, a state of affairs which as we progress, we shall find is characteristic of other constituents of the metals we are considering.

Much might be said in regard to the color test for determining carbon in steel. It is difficult to over-estimate the value and importance of this method, especially in the daily operation of steel works, and there seems little doubt but that if proper precautions are employed, the method in skillful hands will give results that are fairly reliable to within three or four-hundredths of a per cent. It would hardly be possible in this paper to discuss all the precautions which are deemed essential by those best informed. A chemist of wide experience with the method, has enumerated twenty-four points that must be observed, if reliable results are to be expected. Let it suffice for us to say that even approximate accuracy cannot be expected.

1. If the steel whose carbon is to be determined and the standard steel do not have their carbon in the same condition. For example, if the standard steel has been annealed, and the sample to be tested has been tempered, the results will be worthless.

2. If the attempt is made to determine the carbon in any steel by using a standard widely different from it, in carbon content. Using a 0.20 per cent. carbon standard, with a steel containing 0.50 or 0.60 per cent., is apt to lead to very fallacious results.

The best results seem to be obtained by having the carbon in all steels both standards and tests in the condition given by annealing, by having a number of standards which differ little from each other in carbon content, and by not attempting to use the method on steels containing very little or very large amounts of carbon. It may not be amiss to add here that the practice so prevalent in many of the steel works, of using this method for all carbon determinations, including those where contracts are involved, is reprehensible and should be discontinued. The chemist at the works does the best he can with the method he is using, and the amount of work required of him, as well as the facilities furnished, do not admit of the use of a better method. On the other hand when a dispute arises, and it is ultimately shown that the works are in error, the chemist is blamed and analytical chemistry brought into disrepute, not because either is really at fault, but because more is expected of the color test method, than it is really able to give. To the steel makers we say, "Do not expect your chemist to render you the bricks of good chemical analyses, without you give him the requisite straw of time and appliances to do good chemical work."

Few of the constituents of iron and steel have more important influences on their valuable qualities than phosphorus, and upon few has more chemical work been done. The present condition of the methods for determining this constituent, seems fairly satisfactory provided we are willing to take time enough to do the work. In confirmation of this statement, the work<sup>1</sup> done by the Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel may be cited. This sub-committee consisted of five members, each of whom analyzed five samples of steel, and each used his own method, without any

<sup>1</sup> *Proc. Am. Soc. Civil Eng.*, 21, 59.



attempt at consultation or agreement with each other before the work was done. The methods employed may be briefly indicated as follows, those interested being referred to the report of the committee published as per the reference given for the details. Mr. Blair used what is known as the acetate method. Mr. Shimer used the molybdate magnesia method. Your speaker used a combination of the acetate and molybdate magnesia methods. Dr. Drown used a combination of certain features of the modern rapid methods with the molybdate magnesia method. And Mr. Barba on one sample used the acetate method as described by Blair, and on the other four samples employed certain features of the molybdate method to separate the phosphorus from the iron, and then used the reductor to get the amount of phosphorus, instead of weighing as magnesium pyrophosphate. It will be evident to any one carefully reading the report referred to, that the methods employed differed widely in principle, in strength of solutions, and in manipulation, and yet these methods gave the following percentages of phosphorus in the five samples :

	1.	2.	3.	4.	5.
Mr. W. P. Barba.....	0.041	0.015	0.095	0.091	0.041
Mr. A. A. Blair .....	0.040	0.016	0.098	0.091	0.041
Dr. T. M. Drown ....	0.042	0.016	0.104	0.090	0.042
Dr. C. B. Dudley ....	0.040	0.016	0.099	0.097	0.039
Mr. P. W. Shimer....	0.041	0.017	0.098	0.096	0.039

In explanation of the results, we quote from the report of the sub-committee.

“Sample No. 1 is an ordinary open-hearth steel. Sample No. 2 is a crucible steel. Sample No. 3 is an open-hearth steel to which metallic arsenic was added while in the molten condition in a crucible. Sample No. 4 is an ordinary Bessemer rail steel. Sample No. 5 is the No. 5 sample of the Committee on International Standards, and is an open-hearth steel.

“It will be observed that the agreement in the results on phosphorus obtained by the different chemists is very good. The exceptions are the No. 3 steel, which contains arsenic in considerable amount, and where the discrepancy is 0.009 per cent., and in the No. 4 steel, where the discrepancy is 0.007 per cent. Considerable work was done on the No. 4 sample, in an effort to reconcile discrepancies, and it was found that the turnings from this

sample were irregular, and that two different bottles of the sample gave different results. The average of six determinations from one bottle was 0.1057, and the average of five determinations from another bottle was 0.0964 per cent. Furthermore, siftings from quite an amount of the turnings gave 0.140 per cent."

But these methods are long and laborious. It would be impossible with the most rapid of them to get a result in much less than a day, while two days would certainly be required for some of the others. Accordingly, since the demand for rapid phosphorus determinations during the last ten or fifteen years has been very great, an enormous amount of work has been done in trying to meet this demand. Modification after modification has been introduced, and paper after paper published on the subject. It is perhaps not too much to say that few chemical journals that publish any original work at all, have escaped three or four articles per year, on the determination of phosphorus in iron and steel, or on some phase of a rapid method for such determination. The result of all this work has apparently been constantly increased rapidity, with constantly greater approximations to accuracy. The present state of the matter is perhaps best shown by Thackray<sup>1</sup> in his paper, "A Comparison of Recent Phosphorus Determination in Steel." This writer sent to some twenty-three different chemists borings from two different samples of steel, with a request to have the phosphorus determined in each sample, and a description of the method used sent with the results. Each chemist was told that samples had been sent to others, but no attempt was made to have any special method used. The chemists embraced a professor in a technical school, the chemist of a large consumer, a number of commercial chemists, and a number of chemists employed by steel and iron works. On one sample thirty-six different results were sent in, and on the other thirty-eight. Twenty-seven different methods were employed, some of the chemists sending in results by two, and even three methods, and some sending duplicate determinations. The results obtained were obtained as follows, the figures being percentages of phosphorus in the steels:

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 25, 370.

Sample.	1.	2.
Average of all determinations.....	0.0496	0.0835
Highest result.....	0.055	0.091
Lowest result.....	0.045	0.076
Maximum difference.....	0.010	0.015

The methods employed may be divided on the basis of time required into three classes:

1st. Those which may be called rapid, and which give a result in two hours or less.

2nd. Those which may be called slow, and which require considerably more than two hours, but still give a result the same day.

3rd. Those which may be called very slow, and which do not give a result until the second day or later.

Thirteen results on each sample were given by "rapid" methods, eleven on the No. 1 sample, and twelve on the No. 2 sample by "slow" methods, and twelve on the No. 1, and thirteen on the No. 2 by "very slow" methods. Arranging the results in accordance with this classification of the methods (and we have some very interesting data), the figures being as before, the percentages of phosphorus in the two steels are:

	Rapid methods.		Slow methods.		Very slow methods.	
	1.	2.	1.	2.	1.	2.
Average of all determinations	0.0499	0.0840	0.0490	0.0826	0.0496	0.0837
Highest result.....	0.054	0.091	0.052	0.086	0.055	0.089
Lowest result.....	0.045	0.078	0.046	0.076	0.046	0.078
Maximum difference.....	0.009	0.013	0.006	0.010	0.009	0.011

To our minds these figures are very impressive. It is worthy of note—

1st. That the average results given by the "rapid" methods only differ on either steel from the averages given by the "slow" or "very slow" methods, by a little over 0.001 of a per cent.

2d. That the maximum difference between the highest and lowest results given by the "rapid" methods on either steel is but a trifle greater than is shown by the "slow" or "very slow" methods.

In other words, if we interpret these results correctly they show that the rapid methods for determining phosphorus in steel now known and in use in many laboratories give results that are well nigh as accurate and reliable as those yielded by the longer and more laborious methods, and it must not be forgotten that

although we have placed two hours as the time characterizing a rapid method, a number of the results given above were obtained by the use of methods which give a single determination in forty-five minutes, and enable one operator to make twenty phosphorus determinations in a day. We are frank to say we do not believe such a showing would have been possible five years ago.

But these results still leave something to be desired. The discrepancy between the highest and the lowest result, is still too great. It is, perhaps, a little hazardous to place limits, but we do not think the chemists of the country should be satisfied until they are in possession of a method or methods which are so carefully worked out and so well described that in the hands of different chemists of good, fair ability and experience, results will be obtained by all, when working on the same steel, that will not differ from each other more than 0.003 per cent. The Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel before referred to, have had in hand now for some two years, studies on a rapid and accurate method for the determination of phosphorus in steel. It has been the hope of the sub-committee that the ideal above given would be attainable by this method. In reality, the work of the sub-committee has embraced an examination of almost every chemical point involved, taking very little if anything for granted, and checking and proving every step. The work is not yet quite ready for publication, one or two points remaining which are not entirely settled, and it has been deemed advisable to withhold the method until these are completely cleared up.

Some years ago, with the publication<sup>1</sup> of what is commonly known as Ford's method, the determination of manganese took a decided step forward, at least in this country, so far as speed is concerned. Previous to that time the long and laborious acetate method which involved the separation of the iron from the manganese as basic acetate and subsequent precipitation of the manganese by means of bromine or as pyrophosphate, had held full sway. Ford's contribution consisted, as is well known, in separating the manganese from hot nitric acid solution of the iron or steel, by means of potassium chlorate, and Williams<sup>2</sup>

<sup>1</sup> *Trans. Am. Inst. Mining Eng.*, 9, 397.

<sup>2</sup> *Trans. Am. Inst. Mining Eng.*, 10, 100.

added the modification, now in common use, of determining the separated oxide of manganese, by its action on a standard solution of ferrous sulphate or oxalic acid. This method as now worked in many laboratories, gives a single result in forty minutes and two in an hour, and enables one operator to turn out twenty to twenty-five determinations in a day. The accuracy of this method has been questioned. We are not aware of any recent symposium on manganese, where different chemists using different methods, have worked on the same steels. In our hands this method gives results closely agreeing with check work done by the more laborious and generally accepted accurate methods, provided the sample contains not more than three-fourths of a per cent. On samples containing over one per cent. of manganese, the results are apt to be low, owing probably to the fact that the manganese does not separate from the nitric acid solution as manganese dioxide, but as some other oxide, whose composition is not positively known. In the calculation it is customary to regard the separated oxide as manganese dioxide, and this leads to perceptible error on large amounts. Producers and consumers rarely contend much over manganese in steel, and methods for its determination have perhaps not received, on that account, all the attention they deserve. There is evident need of more work on this subject.

The methods for the determination of silicon can hardly be regarded as in a perfectly satisfactory condition. If evaporation to dryness to render silica insoluble, is employed, the time required is considerable. If dehydration by means of sulphuric acid and heat, as suggested by Drown<sup>1</sup> is employed, there are difficulties which interfere somewhat with accuracy. There seems little doubt, but that in skilled hands, with sufficient care taken in the manipulation, a couple of determinations may be made on the same sample, using Drown's method, that will agree closely with each other, and with results given by the longer and more laborious methods. On the other hand, where one operator is making a number of determinations at the same time, there is much danger of error, due either to failure to dehydrate sufficiently or to overheating, resulting in the formation of insoluble iron salts. Our experience indicates that the margin between

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 7, 346.

these two extremes is not very wide, and that it is fully as frequent to have duplicates on the same sample disagree as to agree. Our observations point to the view that the difficulty of insufficient dehydration is due to the separation of iron salts, as the sulphuric acid concentrates. These salts enclose gelatinous silica, and prevent the dehydrating acid from getting at it. Unless great pains are taken, therefore, to secure this contact by sufficient stirring, the results will be low. If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method. It may not be amiss here to call attention to the fact first noticed in the laboratory of the Pennsylvania Railroad Company,<sup>1</sup> that after the dehydration and subsequent dilution are finished, if an interval of a few hours is allowed to elapse before filtration, the silica will redissolve and the results be low. Apparently as we are able to work the method, the silica is not completely dehydrated, but only sufficiently so that if filtered at once, fairly accurate results will be obtained.

It is difficult to say anything positive about the speed and output of Drown's method. It is probably safe to say that a couple of determinations could be made in an hour and a half, but, on account of the difficulty mentioned above, the method does not lend itself well to working on a large number of samples at once, and consequently a large daily output is somewhat interfered with.

It must also be said of the methods for the determination of sulphur in iron and steel, that those most in use are hardly as satisfactory as could be desired. The studies of Phillips<sup>2</sup> conclusively show that when using the evolution method, the whole of the sulphur content is not given off in such a form as to be retained by the usual means employed to catch the gas. It seems not too much to say that it is hazardous to use the evolution method on pig or cast iron, even when fusion of the residue is employed. The formation of unoxidizable gases containing sulphur, in the application of the evolution method to steel, has

<sup>1</sup> Address to the members of the Chemical Section of the Engineers' Society, at Pittsburgh, September 27, 1892, by C. B. Dudley, on "Discrepancy in Chemical Work by Different Workers."

<sup>2</sup> This Journal, 17, 891.

not, so far as our knowledge goes, yet been demonstrated, and accordingly the evolution method is still used largely on steels. But on pig and cast irons the oxidation method seems the only one applicable and some recent studies of Blair, described in a paper at this meeting,<sup>1</sup> indicate that on certain pig irons, all the sulphur is not given, even by this method, unless the graphitic residue is fused with sodium carbonate and niter. Both methods are somewhat slow, and there is need of further study. If some means could be found by which barium sulphate could be readily and accurately converted into sulphide so that a volumetric method could be applied to this sulphide, it would be a decided step forward. The necessity in accurate work for purifying barium sulphate, as first obtained from almost any solution, by fusion and reprecipitation, adds quite considerably to the time required. With steels and two sets of evolution apparatus, using bromine for oxidation, two determinations may be made in two hours. With four sets of evolution apparatus, one operator can make twelve determinations in a day. In these cases purification by fusion is not attempted. By the oxidation method on pig or cast iron, two determinations require about five hours, while one operator with a supply of borings ahead and sufficient appliances, can get from ten to twelve results in a day. With this output, purification by fusion is not attempted. If this is done, the time for a pair of determinations must be extended an hour and a half, and the daily output would be cut down at least a third.

From what has preceded in this hasty and necessarily imperfect survey of a portion only of the analytical methods in use in the iron and steel industry, it is clearly evident that there still remains an enormous amount of work to be done in connection with methods. We have touched upon only five of the fifteen or twenty constituents occurring in and affecting the quality of iron and steel, and find the methods for determining even those more or less imperfect, and needing more work. What will be our condition as chemists if, as seems probable, nickel, chromium, aluminum, tungsten, and the gases, oxygen, hydrogen, and nitrogen, either free or combined, within the next few years, come into prominence as constituents of iron and steel, and are made elements in important commercial contracts? Still further, thus

<sup>1</sup> See page 114 of this issue.

far our methods are concerned almost entirely with the total content of the various constituents we are determining. We know very little about the compounds of the various constituents occurring in iron and steel, with the metal or with each other. Is the phosphorus present as phosphide or phosphate, or both? How besides as sulphide does the sulphur occur? Do the various carbides which are revealed by the microscope, and which are believed to be so closely dependent on the heat treatment which steel receives, and which are so intimately related to the value of the metal, differ from each other in carbon content, or only in crystalline form? Who will be the first to isolate any of these carbides? Who will first give us a practicable, accurate and sufficiently rapid method for determining oxides in steel? Who will first completely investigate the relation between the chemistry and the chilling properties of cast iron? And who will first give us a study on the form in which nitrogen occurs in this metal, and a sufficiently rapid and accurate method for its determination? Truly the harvest of chemical work before us in connection with iron and steel is bounteous. Will the laborers be forthcoming to gather the harvest?

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

### XLIX. SOME PECULIAR FORMS OF IRON.

By T. H. NORTON.

Received January 18, 1897.

I HAVE recently had occasion to examine two rather odd forms of iron, the peculiarities of which are sufficiently marked to warrant a brief note. The first of these is a sample from a mass of pig iron taken from a deep crevice in the hearth of a blast furnace at Ætna, Tenn., after the furnace was blown out. The conditions were such that the iron had been maintained in the molten condition for over a year, and had then cooled and solidified very slowly.

In appearance the sample is of a light, silvery color, and exhibits a most marked crystalline structure, with rectangular cleavage. Despite this crystalline character, it is the reverse of brittle, and shows a high degree of malleability, fragments being easily flattened out with a hammer. The drill makes but slight