the ferrous sulphate solution may be changed to meet special cases.

I am surprised that this method has not come into general use, for it combines in a remarkable degree extreme accuracy and great rapidity with simplicity and ease of manipulation.

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THE DETERMINATION OF SULPHUR IN IRON.

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A PAPER on this subject by the same authors was read before the American Chemical Society at its meeting in Cleveland in June, 1903, in which paper the authors took a somewhat different view of the subject, in part at least, from that ordinarily taken, and expressed the opinion that this or that method was not responsible for all the trouble experienced in getting close checks on sulphur determinations, but that much of the trouble was due to the analyst through carelessness, inability or inexperience.

In the present article the substance of that paper will be used, rewritten in part, together with some additions based on the results of further experiments.

We wish to emphasize the fact as pointed out in the paper mentioned that the determination of sulphur in iron is as difficult probably as any the iron chemist is called upon to make, and the young man of limited experience who may perchance have trouble with it must by no means feel that his career as a chemist is ended, and we also wish to say that we believe there is much to be said in regard to the relative merits of different methods—which phase of the question will be considered later—but at the same time we firmly believe that a competent chemist should be willing to sign his reports with his name instead of the method he used. We would not decry the principle of standard methods, as in the main they are excellent, but a too rigid application of that principle tends to relieve the analyst of responsibility—this too when the personal element cuts so large a figure that two operators using the same method described in minutest detail (and this is particularly true

of sulphur methods) may and often do obtain widely varying results. We believe a careful chemist should (especially in cases of dispute) check his work by different methods, and so prove his results up and down and crosswise that he is practically sure they are within the limits of a reasonable error of manipulation. In this case the "method" will very seldom be asked to stand responsible for failures.

In a number of instances where we have disagreed with pig-iron manufacturers and have had occasion to submit samples to other chemists, we have found that works chemists, or those employed by and working exclusively for manufacturing concerns, generally checked us, while commercial chemists were generally low. We believe this can be very generally accounted for by the fact that the actual work in commercial laboratories is turned over to inexperienced or incompetent men and not at all that the heads of the firm are not first-class chemists. Nevertheless, these results turned out by commercial chemists of high standing make lots of trouble as we have had occasion to know, since they are generally accepted on the standing of the firm. We would not wish to be understood by this that works chemists are better as a class or that they are more conscientious workers, but they have more experience with this particular line of work, and, moreover, any mistakes which they make would come back on them in a way which would be disastrous to themselves. For these reasons we do not think it strange that they are, as a rule, more reliable in their own special line of work.

In every such instance the commercial chemist was not condemned until our results were proved, not only by other chemists but by different methods and in every way possible.

As to methods, there are, as every one knows, two general methods—the evolution and the oxidation. The evolution method will not be considered in detail in the present paper, since it is properly used only under certain conditions and as an adjunct to the oxidation method upon which it depends directly or indirectly for its accuracy. It bears about the same relation to the oxidation method that the color method bears to the combustion method in the determination of carbon. In using this rapid method on any fairly uniform grade or brand of iron, we believe the better way is to standardize the iodine solution against a sample of the same

iron, in which sample the sulphur has been accurately determined by the oxidation method. In this case the theoretical value of the iodine solution may or may not be correct, according as this particular iron does or does not give off all its sulphur as hydrogen sulphide, but the sulphur value of iron of like character given by the direct reading will be quite accurate.

The method is by no means universal, and a standard solution once adjusted to a certain kind of iron can not safely be used on irons of different or unknown chemical and physical characteristics. Such use, however, we know is too often made of this method and we wish to say in this connection that while it has a wide and legitimate use in iron and steel works it has no place in a commercial laboratory. At least it should never be used in cases of dispute or where the general nature of the sample submitted is unknown.

Considering then, more particularly, the oxidation method, it is clear to a reasonably close observer, even where the integrity and ability of the analyst is above question, that there is much difficulty in obtaining close checks on sulphur determinations and that the sulphur content is too frequently in dispute. If one inquires as to the method used, in say a dozen analyses where the variations in sulphur may be far outside the allowable limits of accuracy, it would probably be found that the oxidation method had been used in most cases. That is, this method had been followed in general, though its variations in detail are many and probably no two samples had been treated exactly alike.

It appeared to us that there should be more certainty and accuracy in this work, and it was the various details of the oxidation method that we first worked upon, with a view of ascertaining their relative importance.

The essential features of the oxidation method as commonly published and used to-day are: The solution in a beaker or dish of the drillings in strong nitric acid, generally with the addition of some hydrochloric acid and a little sodium carbonate; baking, after evaporation to dryness; solution in hydrochloric acid and again evaporating to dryness and baking; dissolving again in hydrochloric acid, addition of water, filtering and precipitating with barium chloride in this filtrate, which according to various authorities should be anywhere from 75 to 300 cc. in volume. There

is no question that this manner of handling the method gives low results in a large majority of cases, and the trouble we believe to be largely in the loss of sulphur in the too rapid solution of the drillings. We were by no means the first to discover this, since for some years a device (the idea, we believe, of Mr. Brady, chief chemist of the Illinois Steel Company, South Works) has been in use in that laboratory, consisting in inverting a small watch-glass over the borings in the bottom of a casserole before putting on the acid. When solution begins, the escaping gases are held under the watch-glass until enough collect so that their buoyancy tilts it up and allows them to escape, but not until those carrying sulphur have been held in contact with the oxidizing gases some time. Care must also be taken to only warm the dish sufficiently to cause solution to take place slowly.

We have made many determinations with and without the watch-glass, all other parts of the operation being the same, and have proved that the watch-glass will give higher results.

We give below some figures showing the sulphur obtained with and without the watch-glass, on the same samples.

No.	Kind of iron.	With watch-glass. Per cent	Without watch-glass. Per cent.
1	Gray cast iron	0.112	0.103
2	" " "	0.143	0.131
3	" " "	0.134	0.113
4	" " "	0.137	0.113
5	Malleable Bessemer pig	0.045	0.038
6	" " "	0 047	0.037
7	No. 2 foundry pig	0.018	0.023
8	" " "	0.036	0.030
9	" " "	0.044	0.019
10	Bessemer steel	0.080	0.071
11	" "	0.073	0.075

On two or three of the samples it will be seen that the amount of sulphur obtained without the use of the watch-glass, checks or slightly exceeds that obtained when using it, while in one case, No. 9, the difference is exceptional. This varying difference is characteristic, since the loss of sulphur when dissolving rapidly in an open dish is greater or less according to the strength of the acid, rapidity of solution and possibly the character of the iron. Under some conditions there is no loss, but there is no certainty in regard to this.

Thinking it would be well to prove positively that sulphur was driven off by rapid solution, a 1000 cc. flask was fixed up in the same manner as for volumetric determinations, in which the borings were dissolved as rapidly as possible with strong nitric acid and the escaping gases passed through different absorbing solutions, but we could obtain no trace of sulphur in the absorption bulbs. The contents of the flask were then treated in the regular way and all the sulphur was found. Inasmuch as the flask was closed during the solution of the borings, with the exception of the small delivery tube, it was filled, of course, with oxidizing gases and it appeared that they completely oxidized and retained the sulphur. Acting on this suggestion, borings were dissolved in a tall Erlenmeyer flask with a funnel set in the top which compelled the evolved gases to circulate pretty thoroughly in the flask before passing out. The contents of the flask, after solution was complete, were treated by different methods and in all cases all the sulphur was recovered, or at least as much as could be obtained by any other method, with the exception of one sample which was afterwards found to contain titanium. We think these experiments show the importance of bringing the borings into solution slowly and in such a mannner as to keep the escaping gases as long as possible in contact with the oxidizing agents.

Again the addition of the proper amount of ammonium chloride after dissolving the baked mass in hydrochloric acid the last time, just before filtering, is important, since, if properly manipulated, it leaves the filtered solution just acid enough and with enough ammonium chloride so that the complete precipitation of the barium sulphate, entirely free from iron, is assured.

The practice with the authors is to take up the baked mass from a 2-gram sample in 10 cc. strong hydrochloric acid. Heat this to dissolve the iron salts and at the same time evaporate the solution to from 4 to 5 cc., then add 5 grams ammonium chloride. This amount of ammonium chloride will nearly or quite absorb the hydrochloric acid, if the evaporation has been carried far enough, and after the addition of water and filtering and washing will leave the filtrate about 75 cc. in bulk and with a sufficient amount of ammonium chloride and free acid for complete precipitation.

Another method of preparing the filtrate for the precipitation of the barium sulphate is that of Lunge modified by Küster and

Thiel[1] and used by Hillebrand and others, though not applied to any great extent in the determination of sulphur in iron. In this case the baked mass is dissolved in strong hydrochloric acid, diluted with an equal amount of water, filtered and washed. This filtrate is made slightly ammoniacal. 10 cc. barium chloride added, then slightly acidified with hydrochloric acid, diluted to 300 cc., boiled down to 100 cc. and allowed to stand over night. This method of precipitating the barium sulphate has not been used to any great extent by the writers but so far as tried appears to give good results.

Some work was done on the method proposed by W. A. Noyes and L. L. Helmer,[2] but while this method appears to have some advantage over the oxidation method, it is more than offset, we believe, by its disadvantages. It is complicated, and the determining and weighing of the barium sulphate in two different portions is liable to double the ordinary error of manipulation. The necessary fusion of the residue is an objection, we think, as against a method that does not require it. The barium sulphate obtained by this method is very likely to contain silica, and furthermore we disapprove of the "permanent correction" principle as suggested in Professor Noyes' paper. We wish to say, in this connection, that the method of Professor Noyes, as well as that of Küster and Thiel, was tried just as first published. It is probable that extended use and experience might remove some of the features that appeared objectionable to the authors. However, as the general principle and main reactions involved did not appear as promising as those of some other methods, further work on it was not attempted.[3]

Although the details of the regular oxidation method were worked out very thoroughly and although results were obtained repeatedly that checked up with other methods and with other

[1] *Ztschr. anorg. Chem.*, **19**, 97.

[2] This Journal, **23**, 675.

[3] It should be noted that the fusion of the residue in the method of Noyes and Helmer is only required for irons containing sulphur which cannot be brought into solution by the usual methods. Also, that the separate precipitation of the sulphur contained in the fused mass was carried out in order to determine the amount of such insoluble sulphur. In ordinary practice the fused mass could to advantage be dissolved in water and added to the main solution before the latter is precipitated by ammonia. By this modification only a single precipitation of sulphur is required. We are not aware of any experimental evidence to show that silica is carried down with the barium sulphate from a solution in which iron has been first precipitated by ammonia. Indeed, several authors have shown that small amounts of silica in solution do not interfere with the determination of sulphuric acid.—EDITOR.

chemists who were familiar with this line of work, we were still not entirely satisfied, inasmuch as we were convinced that success still depended very largely on a high degree of skill in manipulation—and right here is probably the secret of so many failures.

A method seemed desirable that would allow a little more latitude in manipulation and, at the same time, be reliable and accurate, and from our investigation we believe Bamber's method is worthy of a strong recommendation.

This method was first published, we believe, in the year 1894 in the Journal of the Iron and Steel Institute and has had a limited use since that time, but we do not think it is anywhere near as well or favorably known as it should be. The Journal of the American Chemical Society for February, 1897, contains an article on it, by A. A. Blair[1] and it is also given prominent mention in the fifth edition of Blair's "Chemical Analysis of Iron," but one does not often find it referred to in any book or paper on iron or steel analysis published in the last eight or nine years. The method as we prefer to use it is as follows: A 2-gram sample of drillings is dissolved slowly in nitric acid in a platinum dish, using the inverted watch-glass over the drillings as before described. After the iron is completely dissolved the watch-glass is removed from the solution. 1 gram of potassium nitrate added and the solution evaporated to dryness and ignited over a Bunsen burner at a good red heat for three or four minutes, turning the dish so that the side as well as the bottom is heated to redness. Add 50 cc. of 1 per cent. solution of sodium carbonate, boil for a minute or so, filter, using paper pulp, and wash with hot 1 per cent. sodium carbonate. Acidify filtrate with hydrochloric acid and evaporate to dryness. Take up in 50 cc. water and 2 cc. strong hydrochloric acid, filter, wash, and in the filtrate, which should be about 75 cc. or 100 cc. in bulk, precipitate the barium sulphate with barium chloride.

By this method accurate results can be obtained with certainty and with less fine-haired manipulation than with the oxidation method and it is applicable to many irons that would be troublesome with the ordinary oxidation method. There is no danger of the dry mass taking up sulphur from the flame in the three or

[1] This Journal, 19, 114.

four minutes it is ignited. This method can be worked in about the same, or even less, time than the oxidation method, and we think it preferable.

The following instance will show that others may sometimes get a better result with the Bamber method than with any other though they may not know it. Some time since we disagreed with a blast-furnace company on the analysis of some iron. A large sample was carefully prepared under the joint direction of ourselves and a representative of the furnace, and samples sent to some six or seven chemists. Three of them were commercial chemists of national reputation and the others were employed by large iron and steel manufacturing concerns. The iron was guaranteed below 0.050 sulphur. We found 0.060 and all the works chemists checked us quite closely, their results averaging about 0.057, with none lower than 0.055. The commercial chemists checked each other quite closely at 0.045. Some time after, having in the meantime done some work with the Bamber method. we sent another sample of this same iron, without any comment, to one of the commercial chemists who had previously reported on it, with a request that a sulphur determination be given us by the Bamber method. In due time the report came back stating that this had been done and the result was 0.056. This incident illustrates very concisely two points which we have attempted to make; that the oxidation method will give accurate results if handled by men who understand it, as most iron and steel works chemists do, while those not using it so often and not so thoroughly acquainted with all the necessary and apparently insignificant details will be more likely to get nearer the truth with the Bamber method.

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THE DETERMINATION OF PHOSPHATES IN AQUEOUS EXTRACTS OF SOILS AND PLANTS.[1]

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IN AN earlier paper[2] a colorimetric method for determining small amounts of phosphates in the presence of silica was pre-

[1] Published by permission of the Secretary of Agriculture.
[2] This Journal, **25**, 1056 (1903).