VOL. XVI. APRIL, 1894. NO. 4.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

AN ATTEMPT TO FIND THE AMOUNT OF PHOSPHORUS IN THREE SAMPLES OF STEEL.[1]

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SOMETHING over a year and a half ago, in connection with the preparation of a method for determining phosphorus in steel, to be used as a part of the specifications on which steel is bought, for the use of the Pennsylvania Railroad Company, we deemed it essential to know pretty accurately, the amount of phosphorus in each of three different samples of steel. The use made of the results finally obtained from these steels, is given in our paper, "On Some Points in the Determination of Phosphorus in Steel by the Volumetric Method," and what follows here, is an account of the various efforts made to get the desired information. It will be observed before we have finished, that what at first seemed a very simple thing, proved in the end to be a very difficult affair, and that after all the work done on the subject, the final result is still not entirely free from doubt.

The three samples of steel were as follows: No. 1 was boiler plate made by the open hearth process, and containing presumably about 0.15 per cent. of carbon, and less than 0.05 per cent. of phosphorus. No. 2 was a piece of a locomotive driving tire, made by the open hearth process, and containing presumably from 0.50 per cent. to 0.60 per cent. of carbon and

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[1] Read at the Baltimore meeting, December 28, 1893.

from 0.05 per cent. to 0.07 per cent. of phosphorus. No. 3 was a crucible steel billet, containing presumably from 1.00 per cent. to 1.20 per cent. of carbon and less than 0.04 per cent. of phosphorus. Quite a quantity of drillings from each of these samples was prepared, care being taken to eliminate the influence of segregation as much as possible by (1) putting the drill holes entirely through the sample, and at right angles to the line of final solidification of the metal, (2) by having the drillings as fine as they could conveniently be made, and (3) by thoroughly mixing them.

The drillings having been obtained, our first thought was that we would find out the amount of phosphorus in these steels, by analyzing them ourselves, and by asking some other chemists of recognized ability, to do the same. Accordingly a quantity of the drillings was sent to four different chemists: Mr. A. A. Blair, 406 Locust street, Phila., Dr. T. M. Drown, Mass. Inst. Tech., Boston, Prof. J. W. Langley, Case School of Applied Science, Cleveland, O., and Mr. A. S. McCreath, Harrisburg, Pa. Blair used the acetate method; Drown the molybdate-magnesia method; McCreath the acetate method; Langley both these methods, and we ourselves used the molybdate-magnesia method on all the samples, and the acetate method on the No. 2 sample. We are without information as to the exact details of the methods used by the other chemists. In our own case we used the molybdate-magnesia method, exactly as described in Fresenius' Quantitative Analysis, second American edition, John Wiley and Sons, p. 763, except that we used five grams dissolved in concentrated nitric acid, instead of aqua regia, and heated to 200° C. in an air bath, as suggested by Blair in The Chemical Analysis of Iron, second edition, p. 90, in order to destroy carbonaceous matter. In using the acetate method we proceeded exactly as described in The Chemical Analysis of Iron, by A. A. Blair, second edition, p. 81, and following. We give below the results that have been obtained on these three samples of steel, in accordance with the above, as follows:

				Steel.	
			No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Blair			0.035	0.041	0.029
Another operator			0.035	0.047	0.027
Third operator			0.035	0.047	0.028
Drown, average of duplicates			0.037	0.050	0.030
McCreath		1	0.035	0.045	0.027
		2	0.035	0.046	0.028
Langley	Acetate method	1	0.042	0.053	0.019
	" "	2	....	....	0.020
	Another operator	1	0.042	0.050	0.019
	" "	2	0.042	0.056	0.020
Langley, molybdate magnesia			0.040	0.053	0.022
Dudley and Pease	Molybdate magnesia	1	0.041	0.056	0.033
		2	0.042	0.056	0.032
		3	0.041	0.056	0.033
	Acetate method	1	....	0.047	....
		2	....	0.046	....
		3	....	0.046	....

It will be observed that these results are hardly as satisfactory as could be desired, and that if we must know as we very greatly desired to do, within a couple of thousandths of a per cent. the amount of phosphorus actually in these steels, we were thus far without this information. The extreme variation on the No. 1 steel, is from 0.035 per cent. to 0.042 per cent. a difference of 0.007 per cent. the average of the thirteen determinations being 0.0386 per cent. On the No. 2 steel, the range is from 0.045 per cent. to 0.056 per cent. a difference of 0.011 per cent., the average of the sixteen determinations being 0.0512 per cent. On the No. 3 steel, the range is from 0.019 per cent. to 0.033 per cent., a difference of 0.014 per cent., the average of the fourteen determinations being 0.0262 per cent.

In view of these results some further study was put upon the matter. It will be observed that in our own hands, the molybdate-magnesia method, and the acetate method, do not give the same results, nor do they give the same results in the hands of Langley, and we accordingly were somewhat in doubt, as to which method gave the most reliable results. In order to locate if possible the difficulty, we examined all the residues obtained, in the course of the acetate method, and to our astonishment we found phosphorus in three different places, which we will now describe.

I. It will be remembered that after the phosphorus is separated from the bulk of the iron, by means of the basic acetate precipitate, there is quite a volume of filtrate, containing iron in the protoxide form. This filtrate was allowed to stand in the beaker for a couple of days covered, and at the end of this time, the bottom of the beaker contained quite a precipitate of apparently hydrated sesquioxide of iron, which separated on standing. This precipitate was filtered off, and dissolved in dilute nitric acid and tested with molybdate solution. In no case did we fail to get a little yellow precipitate, apparently indicating that the amount of sesquioxide of iron obtained in the solution, before the basic acetate separation is made, is not quite sufficient to, or does not succeed in carrying down all the phosphorus. The directions require that a few drops of bromine water should be added, to oxidize enough iron to combine with the phosphorus, which was carefully done in every case, but so far as these experiments go, they seem to indicate that some of the phosphorus is still left behind.

II. It will be remembered that the basic acetate precipitate, is dissolved on the filter in hydrochloric acid. In our working of the acetate method, we found in a number of cases, a slight amount of material left undissolved on the filter. On collecting the filters from a number of determinations, burning off the filters, dissolving with nitric acid, and testing with molybdate, a clear reaction for phosphorus was obtained. It should be stated that the stain left on the filter paper, after dissolving in hydrochloric acid, is not in our experience universal. Under certain conditions the basic acetate precipitate apparently goes up with greater difficulty, than with others. It is also claimed that when titanium is present in iron or steel the basic acetate precipitate usually leaves a stain on the filter.

III. The filtrate from the ammonium magnesium phosphate, which it will be remembered contains some iron, and some citric acid, was treated with dilute nitric acid and evaporated to dryness on the steam table. The residue was taken up with dilute nitric acid and treated with molybdate, and here a voluminous yellow precipitate was obtained.

These experiments seemed to indicate that, in our hands at least, the acetate method did not give quite all the phosphorus, and helped to explain the discrepancy between the molybdate-magnesia method and the acetate method. The bulk of the yellow precipitate obtained in the three places above described, especially from the citric acid filtrate, was so considerable that it seemed almost possible to get a sufficient amount of phosphorus from it to weigh, and we accordingly made three more determinations on ten (10) grams each of the No. 2 steel, by the regular acetate method, obtaining as the average of the three 0.045 per cent. The residues from the three places above described from these thirty (30) grams of steel were all collected together and the phosphorus separated from these residues by means of molybdic acid. The yellow precipitate obtained was then treated with magnesia mixture in the regular way. The results gave a percentage of 0.0053 per cent. phosphorus, and this added to the amount obtained by the direct acetate method gave the phosphorus in the No. 2 sample 0.0503 per cent. This figure it will be observed is 0.006 per cent. less than the average which we obtained on the same sample by the regular molybdate-magnesia method.

It has generally been conceded, we think, that the molybdate-magnesia method for determining phosphorus, following Fresenius, is liable to give rather high results, especially if arsenic is present and is not separated, which we did not do. We did separate the possible traces of silica from the magnesium pyrophosphate as Fresenius recommends. We were therefore still in doubt as to the amount of phosphorus in these steels, and did not feel satisfied to use any of the results obtained.

The question therefore arose with renewed force, how shall we find out how much phosphorus these three steels contain? After considerable study and discussion, the following method was decided on, namely: Start with ten grams, and proceed exactly as described in The Chemical Analysis of Iron and Steel, above mentioned, up to the point of adding the bromine. Then instead of adding a few drops, add enough bromine water to convert half a gram of the iron into the sesquioxide. Then make the basic acetate separation as described, except on account of the large amount of iron, a little ammonium acetate is added. Dissolve the basic acetate precipitate in moderately strong hydrochloric acid, and evaporate the liquid to dryness, to render any silica present insoluble. Take up with forty cc. of strong nitric acid, and evaporate to dryness a second time, to remove the hydrochloric. Then take up with seventy-five cc. of dilute nitric acid, 1.13 sp. gr., filter, and precipitate with seventy-five cc. of molybdate mixture, with the proper precautions of the molybdate-magnesia method as to temperature and time. Collect the yellow precipitate on a filter, and after thorough washing dissolve in 2½ cc. of strong ammonia diluted with water, and wash thoroughly with water until the total volume of solution amounts to about 100 cc. Pass hydrogen sulphide until this solution becomes dark red in color. The hydrogen sulphide readily converts the molybdic acid into molybdenum sulphide, in ammoniacal solution, and if the gas has been passed long enough, a complete separation of the molybdic acid results when the solution is treated with hydrochloric acid in slight excess. Filter off from the molybdenum sulphide, wash thoroughly with water containing a little hydrochloric acid, and evaporate nearly to dryness, in order to have controllable bulk of solution. Then take up with a little water, to which two or three cc. of dilute hydrochloric acid has been added, and filter if necessary to remove separated sulphur and a trace of molybdenum sulphide which may separate during the evaporation. Concentrate the filtrate to about fifteen cc., and add five cc. of magnesia mixture, and a little ammonia. The total volume of the solution should not now exceed twenty-five or thirty cc. The ammonium magnesium phosphate from this point is treated in the regular way.

The three samples of steel above referred to treated in this way, gave the following figures:

		No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Phosphorus	1	0.040	0.053	0.032
	2	0.040	0.054	0.033

Unfortunately the separated oxide of iron from the filtrates in the basic acetate separation, in the cases of these determinations were not examined, but subsequent examinations of this material on other samples has shown that half a gram of iron carries down all the phosphorus, or possibly all but the merest trace. Also in the case above mentioned, nothing was left on the filter when dissolving the basic acetate in hydrochloric acid. An examination of the filtrate from the magnesium phosphate precipitate in no case failed to show a slight yellow precipitate, and these results have been confirmed by quite a number of subsequent examinations. The amount of this, however, is very slight, the bulk of the yellow precipitate obtained being very much less than is shown in the citric acid filtrate when the acetate method is used. It seems probable therefore, that notwithstanding all the precautions involved in the method described above, the results given are still a trifle low. These figures were, however, taken as representing the phosphorus content of these three samples of steel.

The method finally used on these steels, and whose results we regard as the most reliable, will be at once recognized as a modification of the combination method, first proposed by Riley, and subsequently described in detail by J. Lawrence Smith in the *American Journal of Science*, **123,** 316. This combination method seems to have several advantages and perhaps to unite, in a sense at least, the best features of the acetate and the molybdate-magnesia methods. The acetate method is used to concentrate the phosphorus from a large amount of material, into a very small amount of iron. The molybdate method is used to separate the phosphorus from the iron. The conversion of the molybdic acid into sulphide in ammoniacal solution is due to a suggestion of Hundeshagen. It will be observed that by the method as we actually used it there are two opportunities to get rid of arsenic, *viz.*, before the basic acetate precipitation is made, and also along with the molybdenum sulphide. Subsequent experiments seemed to indicate that the first of these two separations can be omitted with safety. The method is long and laborious, but seems to offer, all things considered, perhaps the most accurate means now known of determining small amounts of phosphorus in steel. It may be well to add that on coming subsequently to determine phosphorus in these three steels by the volumetric method, a difficulty was found with the No. 2 steel. This will appear by a comparison of the results obtained on the three steels by the two methods, as follows:

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Combination method	0.040	0.053	0.032
Volumetric method	0.040	0.059	0.032

In view of this discrepancy an arsenic determination was made on the No. 2 steel, following exactly the method described in The Chemical Analysis of Iron, p. 188, except that we started with fifty grams. The result obtained was

	No. 2. Per cent.
Arsenic	0.009

This result seems to indicate that arsenic is the cause of the discrepancy in the No. 2 steel, and apparently confirms again the view that arsenic interferes with the determination of phosphorus by means of molybdic acid.

It is perhaps not essential but may not be amiss to say that where the amount of phosphorus is large a difficulty may arise with the combination method, if ten grams are used to start with, due to the large bulk of molybdenum sulphide obtained. Very large amounts of molybdenum sulphide are difficult to wash clean. Of course the difficulty is easily overcome by starting with less than ten grams.

ON SOME POINTS IN THE DETERMINATION OF PHOSPHORUS IN STEEL BY THE VOLUMETRIC METHOD.[1]

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ONE of the most common methods of separating phosphorus from iron, either in ores, pig iron, wrought iron or steel, is by means of molybdic acid, the separation giving rise to the well-known yellow precipitate of ammonium phosphomolybdate. The subsequent treatment of this yellow precipitate is very varied. Some chemists prefer to dissolve the precipitate in ammonia, and then determine the phosphoric acid by means of magnesia mixture. Others prefer to weigh the yellow precipitate just as obtained, and some even to measure the volume of

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[1] Read at the Baltimore meeting, December 28, 1893.