

and bill of lading; and your account is credited £503 2s. 7d., the amount of the invoice and the cost of insurance."

*S. Flewelling, Treasurer, to John Bolton. Dated September 6, 1829.*

"The locomotive engine is on board the *Cornelia*; but could I have known that she would have been so deeply loaded, I should have sent it by the steamboat on Thursday. Capt. Goetchies (?) says there is no hazard; but I shall feel anxious until I hear of its safe arrival, although the wind is moderate, with the prospect of its being fair."

*S. Flewelling, Treasurer, to M. Wurts, Agent. Dated September 12, 1829.*

"The day before yesterday a report was circulated here that the locomotive engine called the *Lion* had by accident been run off the railroad and dashed in pieces. I am glad you mentioned the accident of the wagon running off the road, as it gave me an opportunity of explaining the cause of the report."

*S. Flewelling, Treasurer, to John Bolton. Dated New York, September 15, 1829.*

"Mr. Lord has returned, and says he had the pleasure of seeing you at Kingston. All the persons with whom I have conversed, who have witnessed the moving of the locomotive engines on the railroad, say that they cannot perceive that the iron plates are pressed out of place so as to be any way injurious, and could not discern any damage which they considered important, even after it was pointed out to them."

*S. Flewelling to John Bolton. Dated New York, September 18, 1829.*

"The *John Jay* arrived yesterday, and brings the last locomotive engine. When landed, I shall send it up unless instructed to the contrary."

*S. Flewelling to John Bolton. Dated New York, October 21, 1829.*

"Mr. Dunscomb has put the boiler of the locomotive engine on board the sloop *Forrester*, Captain Betts."

## CONTRIBUTIONS TO PRACTICAL RAILROAD INFORMATION.

### Chemistry Applied to Railroads.

#### SECOND SERIES.—CHEMICAL METHODS.\*

##### I.—PHOSPHORUS IN STEEL—Continued.

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(Continued from page 550, Volume LXVI.)

WITH regard to the method given in the last number, a few words in explanation of the reasons why certain modes of procedure and certain reagents were chosen, rather than others which are likewise in use by good chemists, may perhaps not be amiss.

We have no doubt that many chemists will think that one gram is a small amount to work on, and would prefer to work on a larger amount of steel, thus reducing the possible error. Our decision to use one gram is based on this.

\* The first series of these articles was published in THE RAILROAD AND ENGINEERING JOURNAL, December, 1889-June, 1892. The present article is the third of a new series; the first of these was introductory, the second on the same subject as the present one.

There is a belief, possibly not fully demonstrated, that the complete separation of phosphoric acid from iron is difficult, if not quite impossible, by means of molybdic acid. When we say complete separation we mean the very last and most minute trace. If our memory serves us correctly, eminent chemists have affirmed that such separation was impossible; and the published work of Dr. J. Lawrence Smith—notably his article in the *American Journal of Science*, third series, Vol. XXII, p. 316—seems to indicate that the separation of phosphoric acid from iron is most complete when the proportion of molybdic acid to the iron in the solution in which the yellow precipitate is formed is large. Furthermore, we made this experiment—namely, we took a neutral water solution of chloride of iron and a neutral water solution of molybdate of ammonia, and on mixing these a precipitation ensued of apparently white molybdate of iron, which precipitate is readily soluble in nitric acid. We are inclined to think, therefore, that when the molybdate solution is added to the iron solution in the regular phosphorus determination, molybdate of iron is formed, and that the chances of a complete separation of phosphoric acid are greater, provided the amount of molybdic acid is sufficient to convert all the iron into molybdate. But with the molybdate solution at present in use this result cannot be accomplished without an excessive amount of the molybdate solution, and a very large dilution of the menstruum in which the yellow precipitate is formed, if we start with 2 grams of steel. With the method as we have given it the amount of molybdic acid in the 75 cubic centimeters of molybdate solution is sufficient to convert all the iron into molybdate, and leave a quite considerable excess of molybdic acid to combine with the phosphorus. There are some indications that low results when using the molybdate method may be explained in this way—namely, starting with 5 or 10 grams of steel and only adding the ordinary amount of molybdate solution, the separation of phosphoric acid is possibly not complete. Another series of experiments which we tried also proved instructive. We took a certain amount of nitrate of iron solution containing phosphorus and added 5 cubic centimeters of molybdate solution which contained twice as much molybdic acid as was necessary to precipitate all the phosphorus, everything being done to secure the most favorable conditions for the formation of the yellow precipitate. No yellow precipitate was formed in some time. We then added 5 cubic centimeters more without any precipitation, and so proceeded until we had added 25 cubic centimeters, when the precipitate began to form, and ultimately all the phosphorus came down. Another series with the normal amount of nitrate of ammonia present before adding the molybdate solution showed similar results. Apparently, therefore, a certain amount of molybdate solution, in excess of what is necessary to form the yellow salt, is essential before the yellow precipitate will form in presence of nitric acid and nitrate of iron. Just exactly where the limit is it would require further work to demonstrate; but in view of the uncertainty, we decided on such proportions of metal to start with and of molybdate solution as would convert all the iron and still leave enough molybdate to combine with the phosphoric acid. One consideration further, the permanganate solution given in the method above is of such strength that even though an error of 0.10 cubic centimeter should be made in the readings at the final titration of the molybdic acid, the error introduced by this 0.10 would be but a trifle over 0.0005 per cent. Since, therefore, it is easy to read burettes as close as 0.10, we are inclined to think that the error introduced, even in steels very low in phosphorus, by working on one gram can be safely ignored.

It will be noted that, in the course of the method as described, it is stated that the specific gravities of the solutions are essential. It seems to be generally agreed that the concentration of solutions, the bulk of the solutions, the temperature of precipitation, the amount of free acid present, and also the amount of other salts present, all have an influence on the composition of the yellow precipitate, also that if these conditions are made constant, a yellow precipitate of constant composition or practically so is obtained. It would be, perhaps, too much to say that we have ourselves made experiments to demonstrate each one of these points. We find these points claimed, with more or less demonstration accompanying them, in the literature of the

method, and our experience is limited more especially to the last clause—namely, if we make the conditions constant we have no difficulty in getting uniform results working on the same steel. Duplicate, triplicate and quadruplex determinations on the same steel, on different days, and with different steels, rarely differ more than 0.003 per cent. or 0.003 per cent. on very low steels, provided the directions are carefully followed and the conditions made uniform. Many duplicates show the same result even to 0.001 per cent. It is only, however, by having all the conditions constant that such results can be obtained, and this is why so much importance is attached to the specific gravities of the solutions. It is very interesting to note that dilute nitric acid, even so dilute as 1.135 specific gravity, gives exactly the same results as if concentrated nitric acid was used for the first solution, as we have proven by duplicate determinations on the same sample, using the different gravities of nitric acid to start with. It seems probable that the reaction between the steel and the nitric acid is a complicated one, resulting in the formation of several products. Apparently one of the first reactions, especially if dilute acid is used, is to form a proto-nitrate of iron. The subsequent boiling of the solution after the steel is dissolved converts this, with decomposition of some of the free nitric acid, into the sesqui-salt; and if this boiling is carried out as the directions state, much less of the permanganate will be used in the subsequent oxidation than if the solution is not boiled. It is barely possible that the action of the permanganate may not be completely understood, and there seems a threefold action possible: first, to convert any proto-nitrate of iron that may be left, into the sesqui-salt; second, to oxidize the carbon in the nitric acid solution; and, third, to completely oxidize the phosphorus to phosphoric acid. It is believed that the directions cover the complete oxidation for all steels, but it is obvious with steels containing large amounts of carbon, such as spring steel and tool steel, more oxygen will be used up from the nitric acid and permanganate than from steels containing small amounts of carbon.

The desirability of securing the necessary oxidation of the iron salt and of the carbon, and possibly of the phosphorus to phosphoric acid, by permanganate rather than chromic acid, is a question about which there may be some difference of opinion. In our experience the permanganate seems to accomplish the result fully as satisfactorily as the chromic acid, and does not introduce any free acid into the solution. We have not made exhaustive experiments on the use of these two oxidizing agents, but the method which is especially characterized by the use of chromic acid requires evaporation, which is not essential in the method which we have recommended. Moreover, as will be stated a little later, the amount of free acid present we think has an influence on the composition of the yellow precipitate, and possibly on the amount of it; so that since we can secure the result desired by the addition of the neutral salt, we think it safer and better in every way to do this than to use the free chromic acid. This peculiarity—namely, the use of permanganate instead of chromic acid—is one of the principal differences between the method as we recommend it and Wood's method, which has already been published and largely used. This perhaps is the place to give another reason why we prefer the method as published to Wood's method—namely, in addition to the greater ease and equal certainty obtained by the use of permanganate, we are inclined to think the method that we recommend gives more readily obtained constant conditions than Wood's method. With the latter a certain amount of evaporation to approximately certain bulk of the nitric acid solution is requisite. In our experience, covering now two or three years, we find it very difficult to get uniform conditions as to free nitric acid present with this evaporation. The evaporation itself is a disagreeable operation, is conducted in a beaker not capable of accurate measurement, and results in very concentrated nitric acid, so that a small error of bulk makes a wide difference in the amount of free nitric acid present in the subsequent operation. We have obtained excellent results with Wood's method, but we think the labor and uncertainty of the method are greater than of the method which we recommend.

The amount and strength of the nitric acid used to dissolve the steel and the subsequent manipulation and use of

the solution have been designed in such a way that after the molybdate solution is added the percentage of free nitric acid in the resulting solution is the same as in the molybdate solution itself. Our reasoning was this: It is believed that the yellow precipitate is more insoluble in the molybdate solution than in any other known menstruum, and the insolubility of the yellow precipitate is affected by the amount of free nitric acid. We therefore base our quantities and manipulation so as to secure a final solution in which the yellow precipitate should be formed that would have the same amount of free nitric acid as the molybdate solution. Of course if a molybdate solution can be made in which the yellow precipitate is more insoluble than the one given in the method as published, it would be a step forward. At present, and until further work is done on this point, our method as published rests, so far as the insolubility of the yellow precipitate is affected by free nitric acid, on the amount of free nitric acid in the standard molybdate solution. We of course recognize that the nitrate of iron may have an influence on the insolubility of the yellow precipitate, and our only point here is that, as stated above, so far as the insolubility of the yellow precipitate is affected by the free nitric acid, the method as given assumes that the molybdate solution contains that amount of free nitric acid in which the yellow precipitate is most insoluble.

Those who are familiar with the literature of phosphorus determinations will remember that it has been recommended to reduce the molybdic acid in a flask or beaker by treatment with granulated zinc, and it will be observed that instead of this procedure, we pass the liquid through a reductor containing powdered zinc. We have used both methods, and our experience very greatly favors the reductor method with the powdered zinc. Even with platinum and a little mercury present for amalgamation, the very last portion of the reduction is extremely slow with granulated zinc, and it is difficult to completely discharge the port-wine color. Even a few minutes' standing after the liquid is poured off from the granulated zinc before titration will give this color, indicating incomplete reduction of the molybdic acid. On the other hand, with the reductor the reduction is apparently complete within the first half inch of the powdered zinc in the top, and we have never had the slightest difficulty with any subsequent oxidation. We have run across some parties who claimed that they did not get good results with the reductor, but this is so contrary to our experience that it is difficult for us to see why. We will say, however, that if the yellow precipitate is washed in nitric acid, or in a wash-water containing nitrates, or if all the nitrates are not washed out of the yellow precipitate, there will be trouble subsequently with the reductor. The deleterious effects of nitric acid can be readily demonstrated by any person for himself, by adding a drop or two of nitric acid to dilute sulphuric acid, and passing it through the reductor simply as a blank, followed by subsequent titration. Of course, when nitrates are treated with sulphuric acid, free nitric acid results, producing the same effect. The amount of permanganate used up by even a single drop of nitric acid, under the conditions above, will, we think, astonish any one who has not made the experiment.

It is probable that many chemists will prefer to dry and weigh the yellow precipitate instead of titrating with permanganate, as we recommend, and it is only fair that the reasons which led us to choose the permanganate method should be given. There are two reasons. We may say preliminarily that we have obtained almost identical results by both methods, but in our experience the weighing of any substance on the dried filter is always an operation attended with uncertainty, especially unless one has had a good deal of experience. We have also obtained very satisfactory results by catching the yellow precipitate in a Gooch crucible on an asbestos filter, but find at the best that the gradual change of a dried filter, or a Gooch crucible, during the operation of weighing, is sufficient in our experience to introduce a little feeling of uncertainty as to results. There is another consideration which has some influence here—namely, in steels containing 0.20 to 0.30 of silicon there is always a danger of weighing a little silicon with your yellow precipitate. In view of these uncertainties and in view of the fact that almost every laboratory has or should have a standard permanganate solution which can be easily stand-

ardized and easily kept standard, we finally decided, after a good deal of study and thought, to use the permanganate method. If the reductor is kept in good order and the laboratory has a supply of standard steel or iron, proper care being taken to secure good permanganate of potash and to age it properly before it is used, there are few reagents, if we may trust our experience, that are more satisfactory than permanganate solution.

The end reaction in washing the yellow precipitate may possibly need a word or two of explanation. It will be observed that the directions practically require to allow a few drops of the washings from the funnel to fall into a dilute sulphide of ammonium solution. The wash-water is acid, and the sulphide of ammonium more or less alkaline. It is obvious, therefore, that there may arise two conditions. Enough wash-water may run in to change the sulphide of ammonium solution into an acid solution, or only enough washings may run in to still leave the sulphide of ammonium alkaline or neutral. Under which condition is the greater sensitiveness obtained? Some chemists prefer the acid condition; but our directions call for the alkaline condition, which we prefer, and for the following reason: If we are testing for molybdenum, it is obvious that the acid solution should be used, since molybdenum forms no precipitate in the alkaline solution, but simply changes color slightly. If we are testing for iron, no precipitate or change of color is formed in the acid solution, but a marked change of color results in the alkaline solution. In view of the fact that the yellow precipitate is believed to be slightly soluble in the wash-water if we test for molybdenum, it is obvious we would never get an end reaction, provided the test is sufficiently delicate. On the other hand, we are washing out of the filter molybdate of iron, and when the molybdate of iron is out it is perhaps safe to assume that the filter is washed clean. We accordingly prefer that manipulation which shows the iron, especially since the molybdenum present assists the change of color, even in the alkaline solution.

■ The use of sugar and other organic substances to reduce the binoxide of manganese formed during the process of solution and oxidizing the phosphorus has been proposed. It will be observed that we prefer to use proto-sulphate of iron. It is claimed that there is not much difference between the action of these various substances; and as the amount is quite small, it is probable that the results will not be seriously affected whichever reducing agent is used. We prefer the proto-sulphate of iron, as we do not like to introduce into a steel solution, where we have been trying to get rid of the organic matter, any organic substance. Of course a very large amount of sulphate of iron might produce sulphates enough to interfere with the successful subsequent precipitation of the yellow precipitate, but there seems little danger of this if the directions are followed.

Some questions may arise in regard to the calculations. There is a good deal of variation in the literature of the phosphorus method as to the composition of the yellow precipitate. Our own explanation of these variations is that probably the composition of the yellow precipitate is affected by the conditions under which it is formed. Our figure showing the relation of phosphorus to molybdic acid was obtained as follows: We took three samples of steel, one containing about 0.15 per cent. carbon, one containing about 0.55 per cent. carbon, and another containing about 1.00 per cent. carbon. We made careful phosphorus determinations on each of these three samples by what is known as the combination method—that is, starting with 10 grams, we separated arsenic, and proceeded exactly as described under the acetate method in the "Chemical Analysis of Iron," by A. A. Blair (second edition), up to the point of obtaining the basic acetate precipitate; except that instead of adding two or three drops of bromine to oxidize iron enough to carry down the phosphorus, we added enough bromine to oxidize one-half gram of the iron. This half gram, after being washed on the filter, was treated with nitric acid and the phosphorus separated from it by means of molybdic acid. The yellow precipitate obtained from this precipitation was then dissolved in ammonia and the molybdic acid converted into the sulphide in alkaline solution by passing sulphuretted hydrogen gas, after which the molybdic acid was separated by acid and removed by filtration. In the filtrate concentrated to a very small bulk, the

phosphorus was precipitated by magnesia mixture. The results obtained from these analyses were regarded as the amount of phosphorus contained in the three steels, and the factor used in the volumetric method was based on these analyses.

Within the last year a method of treating the yellow precipitate different from that which we recommend was published by Mr. J. O. Handy, Pittsburgh, which consisted practically in dissolving the yellow precipitate in caustic soda, and titrating the excess of soda by means of nitric acid, using phenolphthaleine as the indicator. This method has been received with a good deal of favor, and, according to our experiments, gives practically the same results as the method which we recommend. Two reasons, however, led us not to adopt this in preference to the permanganate treatment of the yellow precipitate: first, it is more difficult to secure standard solutions of caustic soda and nitric acid than it is to secure a standard solution of permanganate of potash. Starting with metallic iron, the strength of the permanganate solution is easily and quickly obtained, and the same solution is used in almost every laboratory for other purposes. The Handy method requires the maintenance of two special solutions not useful for other purposes. There is another phase of the case—namely, phenolphthaleine is not delicate in presence of ammonia salts; and while the solutions can be so manipulated that this difficulty is small, provided the amount of yellow precipitate titrated is small, we are inclined to fear that with high phosphorus, considerable difficulty would result; so we really saw no advantage in this over the permanganate method, while what advantage there is seems to be the other way, and accordingly we chose the permanganate method.

Also during the past year Mr. H. C. Babbitt, Chemist of the Wellman Iron & Steel Company, Thurlow, Pa., proposed a modification of the method of getting the yellow precipitate, which is claimed to eliminate the co-precipitation of the arsenic with the phosphorus. The method consists practically in precipitating at a temperature not above 25° centigrade. We think it has been taught in some of the schools for a considerable time past that the chances for carrying down arsenic along with the phosphorus by means of molybdic acid were diminished at low temperatures, but it has also been taught that in order to secure a complete precipitation of the phosphorus under these circumstances it was essential to have considerable time. Mr. Babbitt's paper would seem to claim that even at low temperatures and short time, phosphorus might be completely precipitated with the avoidance of the co-precipitation of the arsenic. We have not been able to do much positive work on this question. A little work on a single sample of steel known to contain quite considerable arsenic with considerable phosphorus, does not confirm the view that the phosphorus is completely precipitated at low temperatures and in short time. Further work should be done on this point, and it is fair to say that the question of how to secure the phosphorus in steel by any rapid method without the arsenic interfering, so far as our knowledge goes, is not at present satisfactorily answered. In view of this state of affairs, we decided to take the other horn of the dilemma—namely, to call all that comes down by the method which we have published phosphorus, recognizing at the same time that in steels containing considerable arsenic there is a strong probability that a portion of the material called phosphorus is arsenic. It is barely possible that within the next six months or a year some method of overcoming this difficulty may be devised. It is to be regretted that there is so little positive knowledge of the influence of arsenic on steel. The best authorities that we can consult indicate at least that arsenic is not so harmless an element in steel that it can be ignored, also that its influence is much the same as that of phosphorus; so that, in view of the fact that the steel-makers are forewarned that arsenic will be counted against them, we think no hardship can result.

It will be observed that the method as published is not recommended to be used for pig iron, nor have we experimented with it on ores. It is to be hoped that enough work will be done in the near future to not only check up whatever weak points there may be in the method as it now exists, but also to expand its application.

(TO BE CONTINUED.)