nic, and the deposit has a decidedly violet tint, very distinct from the iron gray deposit of arsenic.

The following distribution of antimony in the two cats may be added:

Acute poisoning (6 hours).	Slow poisoning (72 hours).
Stomach.—Heavy deposit and sublimate. Good test with $\frac{1}{100}$ of stomach.	Good tests.
Liver.—Not so heavy deposit as stomach. Good sublimate.	Heavy deposit and good sublimate.
Heart.—Good deposit after several hours boiling. Good sublimate.	Good deposit on ninety minutes boiling. Good sublimate.
Pancreas.—Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Spleen.—Faint deposit. No distinct sublimate.	
Kidney.—Faint deposit. No distinct sublimate.	Good deposit and sublimate.
Intestine.—Good deposit and sublimate.	Good deposit and sublimate.
Muscle.—Faint deposit on two days boiling. No sublimate.	Slight violet tinge to copper. No sublimate.
Brain.—No deposit.	Marked violet tint to copper. No sublimate.
Spinal Chord.—No deposit.	

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA.

NOTES ON THE DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.

By George Auchy.

Received August 27, 1896.

Of the many improvements made in recent years in the method of determining phosphorus in steel, that of Jones—the use of the "reductor"—is not the least. There has been, however, some difference of opinion as to the completeness of the reduction accomplished by its use. Quoting from three most recent publications on the subject: Doolittle and Eavenson consider the reduction of the molybdic acid to be to a point corresponding to the ratio of 89.16 iron to molybdic acid; Noyes and Royse, by special precautions, obtain a reduction completely to Mo_2O_3 (factor 85.71); and Blair and Whitfield find the ratio 88.16, a reduction to $Mo_{24}O_{35}$ only, even with the precautions of Noyes and Royse observed. Doolittle and Eavenson heat the solution before passing it through the reductor. Noyes and Royse do not. The first named chemists do not use the precautions of Noyes and Royse. It appears from a result by Prof. Noyes given in this Journal, 10, 759, that he does not invariably get a reduction to Mo_2O_3 by his method, his result there given corroborating Blair and Whitfield's hypothesis of a reduction to $Mo_{24}O_{35}$ only.

It was thought by the writer that perhaps the reduction to Mo_2O_3 could invariably be accomplished by combining the precautions of Noyes and Royse with the practice of Doolittle and Eavenson of passing the solution through the reductor hot. The following results were obtained, using yellow phosphomolybdate precipitate dried six hours at 150° C.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0100	1.63	1.63	1.68
0.0100	1.63	1.63	1.68
0.0200	1.63	1.59	1.63
0.0300	1.63	1.63	1.68
0.0300	1.63	1.61	1.65
0.0200	1.63	1.55	1.59
0.0400	1.63	1.59	1.63
0.0500	1.63	1.62	1.67
0.0500	1.63	1.63	1.68
0.0600	1.63	1.63	1.68
0.0700	1.63	1.61	1.65
0.0700	1.63	1.60	1.64
0.1000	1.63	1.63	1.68
0.0400	1.63	1.59	1.63
0.0400	1.63	1.59	1.63
0.0200	1.63	1.58	1.62
0.0400	1.63	1.56	1.60
0.0300	1.63	1.59	1.63
0.0900	1.63	1.57	1.61
0.0400	1.63	1.60	1.64
0.0500	1.63	1.61	1.65

Passing the solution through the reductor hot does not seem to insure an invariable reduction to Mo_2O_3, and perhaps adds nothing to the effectiveness of the process. The following tests were made in the cold :

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.58	1.62
0.0400	1.63	1.59	1.63
0.0300	1.63	1.59	1.63
0.0400	1.63	1.57	1.61
0.0500	1.63	1.63	1.68

But in these last tests, and also in the first series of tests in nearly all cases where the result calculated by Noyes' factor came low, the point of the reductor had been washed off, and the sides of the flask washed down by the jet. Noyes warns against any dilution of the reduced solution before titration, but it was thought that such a slight dilution would do no harm. For a test of this the following determinations were made (cold) and without washing down :

Phosphomolybdate taken. Gram.	Phosphomolybdate present. Per cent.	Phosphorus found. Noyes' factor. Per cent.	Phosphorus found. Blair's factor. Per cent.
0.0500	1.63	1.61	1.65
0.0900	1.63	1.60	1.64
0.0300	1.63	1.61	1.65
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0300	1.63	1.63	1.68
0.0400	1.63	1.60	1.64
0.0400	1.63	1.63	1.68
0.0500	1.63	1.62	1.67

Comparing these results with those of the preceding series it is seen that a complete avoidance of any dilution, however slight, after reduction, will bring higher results than if this precaution be neglected. But it is further seen that the observance of this precaution does not invariably assure a result agreeing with a reduction to Mo_2O_3, although it generally does so. Of the eleven results in the first series of experiments (solution passed through the reductor hot), obtained by an observance of this precaution, seven, calculated by Noyes' factor, are over 1.61 ;

and of the ten results of the last series (reduced cold), seven are 1.61 per cent. or over. On the other hand, of the thirteen results obtained by washing down the sides of the flask after reduction, ten fall short of the theoretical 1.63 per cent. by more than 0.02 per cent., calculated by Noyes' formula, and do bring 1.63 per cent. calculated by Blair's factor. The inability of Messrs. Blair and Whitfield to accomplish a reduction to Mo_2O_3 by an observance of the precautions given by Messrs. Noyes and Frohman, and also the still higher factor found by Messrs. Doolittle and Eavenson, may perhaps be due to the fact that the zinc in each case used differed in reductive power from that of the others. The writer had on one occasion zinc which when used in the reductor with all care and precautions, never gave a reduction of more than one-half; and in his opinion it is safer and more accurate to use the old Emmerton method of reduction and filtration, but with the modifications and precautions described later in this article.

The phosphomolybdate employed in the above tests, was, for part of them, made by precipitating from sodium phosphate solution; for another part of the tests, made by precipitation from pig iron solution, exactly as is done in the determination of phosphorus in pig iron. Messrs. Blair and Whitfield have shown the constancy of the composition of phosphomolybdate made under varying circumstances.

The volume of the solution passed through the reductor in each of the above experiments was 100 cc., as recommended by Blair and Whitfield. Noyes and Frohman use 200 cc., but this seems an unnecessary bulk. Fifteen cc. of sulphuric acid (2:1) was used for acidifying.

For washing 100 cc. of hot water was used containing ten cc. of sulphuric acid, (2 : 1), followed by 100 cc. cold water, and again by fifty to seventy-five cc. of cold water.

The reductor was of the form described by Blair and Whitfield,[1] except that it was considerably wider at the top than the bottom—in shape like a common tin horn. This shape holds more zinc for the given height (ten inches) of the column, and so makes the necessity of filling less frequent.

---

[1] This Journal, 17, 74.

The reductor may be used without refilling till the column of zinc falls to five or six inches without any diminution of effectiveness. All of the results of the two preceding series, and some of the last results in the first series were obtained by the use of five to seven inches of zinc in the reductor.

It adds somewhat to the facility of the working of the apparatus to have the beaker containing the phosphorus solution above the level of the zinc in the reductor so that the connecting tube may work as a siphon. And the last washing may then conveniently be made by diminishing the force of the suction of the pump, loosening the stopper of the reductor, and allowing the water to be siphoned over and fill up the vacant space in the reductor above the zinc column.

The passage of the solution through the reductor was not preceded by the passage of dilute sulphuric acid, and in many of the tests some little air was accidentally drawn over into the reductor at the time of washing, although care was uniformly taken to allow no air to enter at the first washing.

Messrs. Noyes and Royse direct that the reductor should be rinsed with dilute sulphuric acid before using, even if it has stood but a few minutes. This is some little trouble, and to test the necessity of it, the following tests were made :

Phosphomolybdate taken. Gram.	Phosphorus taken. Per cent.	Phosphorus found. Per cent.	Reductor stood.
0.0300	1.63	1.61	one hour
0.0700	1.63	1.60	all night
0.1000	1.63	1.63	six hours
0.0300	1.63	1.63	all night
0.0300	1.63	1.63	three hours
0.0300	1.63	1.63	two days
0.0300	1.63	1.63	two days
0.0500	1.63	1.63	two days
0.0500	1.63	1.62	two days

These results seem an indication that this precaution is not absolutely necessary. But if the reductor stand nearly a week or more, the sulphuric acid will take up considerably more of the impurity of the zinc than ordinarily. Zinc, for instance, which ordinarily will require a deduction of two-tenths cc. from the amount of permanganate used in the titration, will require a deduction of four-tenths if the reductor has stood that length of time unused.

It is necessary to remove the zinc from the reductor at intervals for cleaning, best done by stirring up in a capacious dish with hot water, adding a little sulphuric acid to clear the liquid, pouring off, washing by decantation and drying in the dish on the hot plate. But after such a treatment the zinc, after being replaced in the reductor, should be rinsed with dilute sulphuric acid before being used in analysis, as much more than the ordinary impurity of the zinc will be taken up by the sulphuric acid the first time it is used.

Perhaps a more convenient way of cleaning the zinc is to soak it (in the reductor) in water for a day (conveniently over Sunday), plugging up the ends of the reductor to retain the water. After such a treatment the reductor will go a long time without becoming clogged up with zinc oxide.

Instead of using the reductor, it is a trifle quicker and more convenient, especially when the phosphorus present is considerable as in pig iron, to use the following slight modification of the old Emmerton method of reduction and filtration.

The yellow precipitate in a seven cm. filter paper is dissolved in as little ammonia as possible, allowing to run into the eight-ounce Erlenmeyer flask in which the precipitation occurred; washed five minutes with hot water; the solution acidified with twenty-five cc. of sulphuric acid (two parts water to one part acid); a mustard spoonful of granulated zinc added (five grams), and the flask heated *gently* on the hot plate for five minutes, or until the zinc is nearly dissolved (ten minutes is required for some zinc). The flask is removed from the plate, a little dry sodium carbonate added, and when effervescence has nearly ceased the flask is corked tightly and cooled in cold water without agitating the contents any more than can be helped. The solution is then filtered from the undissolved zinc through a little cotton wool in a Hirsch funnel, smallest size, using the pump, and the flask rinsed out with cold water three times and the rinsings drawn through the cotton wool. The sides of the sixteen-ounce gas flask which receives the liquid are washed down with the jet, and the solution titrated in the flask without further dilution.

If the zinc is of the sort not dissolving very readily, thirty-five cc. of sulphuric acid should be used for acidifying the phosphorus solution instead of twenty-five cc.

The reduction is to $Mo_{12}O_{19}$. Factor of iron to molybdic acid 90.76. More correctly speaking, the reduction is to Mo_2O_3, which filtering and dilution oxidizes to $Mo_{12}O_{19}$.

It will be found upon trial that this way of reduction and filtration is somewhat easier and more rapid than the usual reductor method, as the filtration through cotton wool in a Hirsch funnel and with aid of the pump is performed as easily and quickly as merely pouring and rinsing from one vessel into another. While the zinc is dissolving in one determination, the yellow precipitate of the next determination may be filtered off.

The following results show that the reduction and filtration through cotton wool, as described, brings the molybdenum oxide to the form $Mo_{12}O_{19}$.

Considerable phosphomolybdate (four-tenths to eight-tenths gram) taken for each test.

Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62
1.63	1.62	1.63	1.63
1.63	1.63	1.63	1.63
1.63	1.63	1.63	1.62

Small amounts of phosphomolybdate taken.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Factor 90.76. Per cent.	Phosphorus present, reckoned as if from 1.8233 grams steel. Per cent. in the steel.	Phosphorus found if from 1.8233 grams steel. Per cent. in the steel.
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.63	0.179	0.179
0.2000	1.63	1.65	0.179	0.181
0.2000	1.63	1.63	0.179	0.179
0.1500	1.63	1.64	0.134	0.135
0.0890	1.63	1.62	0.071	0.071
0.0700	1.63	1.64	0.062	0.063
0.0700	1.62	1.63	0.062	0.062

Phosphomolybdate taken.	Phosphorus present.	Phosphorus found. Factor 90.77.	Phosphorus present, reckoned as if from 1.8233 grams steel.	Phosphorus found if from 1.8233 grams steel.
Gram.	Per cent.	Per cent.	Per cent. in the steel.	Per cent. in the steel.
0.0600	1.63	1.64	0.054	0.054
0.0600	1.63	1.63	0.054	0.054
0.0500	1.63	1.61	0.045	0.044
0.0400	1.63	1.64	0.036	0.036
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.64	0.027	0.027
0.0300	1.63	1.61	0.027	0.027
0.0300	1.63	1.60	0.027	0.026
0.0400	1.63	1.62	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0400	1.63	1.63	0.036	0.036
0.0350	1.63	1.62	0.031	0.031
0.0380	1.63	1.63	0.034	0.034
0.0250	1.63	1.61	0.022	0.022
0.0230	1.63	1.61	0.020	0.020
0.0200	1.63	1.55	0.018	0.017
0.0200	1.63	1.51	0.018	0.017
0.0200	1.63	1.64	0.018	0.018
0.0200	1.63	1.50	0.018	0.017
0.0200	1.63	1.60	0.018	0.018
0.0200	1.62	1.55	0.018	0.017
0.0200	1.63	1.57	0.018	0.017
0.0180	1.63	1.55	0.016	0.015
0.0150	1.63	1.55	0.013	0.013
0.0150	1.63	1.55	0.013	0.013
0.0130	1.63	1.51	0.012	0.011
0.0120	1.63	1.63	0.010	0.010
0.0100	1.63	1.51	0.0089	0.008
0.0100	1.63	1.55	0.0089	0.0085
0.0100	1.63	1.46	0.0089	0.008
0.0100	1.63	1.64	0.0089	0.0089
0.0100	1.63	1.64	0.0089	0.0089

The figures in the last two columns were obtained by reckoning as though 1.8233 grams of steel had in each case been taken for analyses. In other words, these percentages in the last two columns are what they would have been had the phosphomolybdate taken been, in each case, obtained from 1.8233 grams of steel, in the regular course of analysis, for phosphorus.

It will be noticed that when the amount of phosphomolybdate taken is very small (equivalent to 0.008 to 0.017 per cent. in steel) there is frequently some oxidation, the percentage of phosphorus in the yellow precipitate thus falling short of 1.63 by as much as 0.17 per cent. in one case. But, as will be seen by reference to the last two columns of results, this affects the result in steel but slightly.

This proneness to oxidation when very little phosphorus is present in the solution indicates that the stability of the $Mo_{12}O_{19}$ solution is greater when concentrated than when dilute. And the solution should therefore be in as small bulk as possible. Other necessary precautions are: to have a large excess of sulphuric acid present, to avoid a boiling temperature when dissolving the zinc, to cool the liquid before filtering from the undissolved zinc, to exclude air while cooling, and to filter rapidly through cotton wool in a Hirsch funnel, with aid of the pump. But where considerable phosphorus is present, as in pig irons, these precautions may be neglected, except the cooling before filtering. That is, the liquid may be cooled, after the reduction with zinc, without the addition of sodium carbonate, and with free access of air, and the filtration may be made through a seven cm. coarse paper (instead of cotton wool) by aid of the pump. The results given under the head " considerable phosphomolybdate taken for each test" were obtained in this way, air not excluded, and filtered through paper instead of cotton wool.

The advantage of making the reduction and filtration in this way in the case of pig iron is very marked when, as frequently happens, the yellow precipitate separates out when its solution in ammonia is acidified with sulphuric acid. For if the reduction be made as described, this separation may be ignored as in contact with the zinc and sulphuric acid the yellow precipitate becomes reduced and goes into solution. This is shown by the following tests, in which no ammonia was used at all. That is, the yellow phosphomolybdate precipitate was weighed directly into the reducing flasks, and thirty-five cc. of sulphuric acid (2:1) poured over, a mustard spoonful of zinc added, heated gently, etc.

Phosphomolybdate taken. Gram.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
About 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63
" 0.4000	1.63	1.62
" 0.4000	1.63	1.63

In experimenting with this process some interesting results were had. The port wine $Mo_{12}O_{19}$ solution is apparently not so stable, especially in dilute solution or with small amounts of phosphorus present, as Emmerton supposed, and certain precautions are necessary.

In the first place considerable amounts of phosphomolybdate were taken, dissolved and reduced as described, and filtered through seven cm. filter papers by aid of the pump. The results showed 1.63 per cent. phosphorus, the theoretical amount.

Several tests were then made in the same way and with the same weights of yellow precipitates, but not waiting for the solutions to cool before filtering from the undissolved zinc. Instead of the theoretical 1.63 per cent., 1.57 per cent., and 1.58 per cent. were obtained, showing the necessity of filtering cold.

Next the stability of the reduced solution was tested.

Before filtering from the undissolved zinc.	Phosphorus present. Per cent.	Phosphorus found. Per cent.
Stood two hours	1.63	1.59
" " " and poured back and forth four times	1.63	1.55
Stood one hour	1.63	1.59
" one-half hour	1.63	1.61

The flasks were not corked while standing.

Smaller weights of phosphomolybdate precipitate were then taken. The results obtained fell very much short of the theoretical, 1.63 per cent., and varied considerably. It was at first thought that the filtration by aid of the pump oxidized the solutions more than by the original Emmerton way of filtering through a large ribbed filter. But, upon making four tests and filtering in that way (Emmerton's) the results gave 1.51 per cent., 1.52 per cent., 1.46 per cent., and 1.48 per cent., respectively, instead of the theoretical, 1.63 per cent., although about four-tenths gram yellow precipitate, was in each case taken; an amount of yellow precipitate which, when taken for the foregoing tests made by filtering through a seven cm. filter paper by aid of the pump, never failed of bringing a result equal to the theoretical. In filtering through a seven cm. filter by the pump the oxidation of the solution is therefore considerably less than the oxidation by filtering through a large ribbed filter.

An article by Blair and Whitfield[1] contains a description of an experiment made by reducing the phosphorus solution by boiling with zinc, keeping an atmosphere of hydrogen continually in the flask, and boiling till the zinc was completely dissolved; then cooling (maintaining the atmosphere of hydrogen in the flask) and titrating, the result falling considerably below the theoretical. In the case of the writer's low results just spoken of, obtained by filtering through a seven cm. filter paper by suction, the reduction had also been effected by boiling with the zinc, though not in an atmosphere of hydrogen, and not to complete solution of the zinc. Remembering the experiment of Blair and Whitfield, above quoted, it was thought that the reason for the low results in both cases lay, perhaps, in the boiling of the phosphorus solutions while being reduced, the sulphuric acid having an oxidizing effect perhaps in that case. No other reason could be offered at least for the low result in Blair and Whitfield's experiment, since, in that experiment, air had been so carefully excluded from the flask during the solution of the zinc and the cooling of the liquid. To test the matter, other determinations were made exactly as before, except that the zinc was dissolved at a gentle heat instead of by boiling. Results were much better, as will be seen in the following table. Hence the necessity for the precaution of avoiding a boiling temperature while dissolving the zinc.

Phosphorus present—1.63 per cent.

---

[1] This Journal, 17, 757.

Phosphomolybdate taken. Gram.	Zinc dissolved by boiling. Phosphorus found.	Zinc dissolved at a gentle heat. Phosphorus found.
0.0100	1.37	1.55
0.0200	1.37	1.50
0.0200	1.37	1.41
0.0300	1.31	1.46
0.0300	1.37	....
0.0400	1.46	1.55
0.0500	1.39	1.57
0.0600	1.28	1.60
0.0700	1.52	1.57
0.0700	1.53	....
0.0800	1.16	1.57
0.2000	1.58	1.63
0.1000	1.59	1.64

In the second column of results, the third and fourth results are considerably lower than the rest of them. But it had been noticed that in these two determinations the green color of the reduced phosphorus solution had faded to the port wine shade during the cooling of the liquid and before the filtration from the undissolved zinc, while in all the other determinations the green color had persisted till the moment of filtration. This pointed to the necessity of excluding air during the cooling of the liquid, preparatory to filtration, from the undissolved zinc, and the precaution was accordingly adopted of corking the flask while cooling,first adding a little sodium carbonate to fill the flask with carbon dioxide. Results by this procedure follow.

As the flask is already filled with hydrogen gas from the solution of the zinc, and vapor from the heating of the liquid, it is perhaps unnecessary to add the sodium carbonate at the end of the reduction. In that case the flask should be corked with a one-hole cork with drawn-out glass jet, during the solution of the zinc ; and the jet closed when the reduction is completed.

It was thought that results agreeing more closely and uniformly with the theoretical might be obtained by filtering through cotton wool instead of paper, as the filtration can be considerably more quickly accomplished in that way, even when much suction is used in the latter way. Results showed this to be the case, and are also given below in comparison with results by filtering through paper.

Phosphomolybdate taken.	Phosphorus present.	Filtration through paper. Phosphorus found.	Through cotton wool. Phosphorus found.
Gram.	Per cent.	Per cent.	Per cent.
0.0100	1.63	1.41	1.55
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0100	1.63	....	1.64
0.0100	1.63	....	1.46
0.0200	1.63	1.46	1.50
0.0200	1.63	1.48	1.60
0.0200	1.63	1.48	1.64
0.0200	1.63	....	1.63
0.0200	1.63	....	1.55
0.0200	1.63	....	1.57
0.0300	1.63	1.58	1.64
0.0300	1.63	1.57	1.63
0.0300	1.63	....	1.64
0.0300	1.63	....	1.61
0.0400	1.63	1.55	1.64
0.0400	1.63	....	1.62
0.0500	1.63	1.57	1.61
0.0600	1.63	1.57	1.64
0.0600	1.63	1.60	1.63
0.0700	1.63	1.60	1.63
0.0800	1.63	1.62	....

From these results it is seen that cotton wool is much better for use in filtering from the undissolved zinc than paper. Very little pressure is required with the former and very little cotton wool is required. A small Hirsch funnel is necessary. But the cotton wool should not be pressed down with the finger after it is wet, but sucked down by the pump. In the above experiments the filtrations through paper were also accomplished by a Hirsch funnel, smallest size. (Paper size, seven cm.)

Using cotton wool, no oxidation of the port wine, $Mo_{12}O_{19}$, solution need be feared where the amount of phosphorus present is that which in a sample of steel (one and eight-tenths grams) would be equivalent to 0.020 per cent. or over; while with percentages under 0.020 the oxidation is never greater than will make a difference of 0.001 per cent. in the result.

All the foregoing experiments were made with the use of zinc, requiring about ten minutes for solution. This supply becoming exhausted, new zinc was procured which happened to dissolve much more freely in acid, and experiments were therefore made as before but using only fifteen cc. of sulphuric acid for solution of the zinc instead of thirty-five cc. as before with the first lot of zinc. Results were noticeably lower, pointing to the inference that a large excess of sulphuric acid present is necessary as favoring the stability of the $Mo_{12}O_{19}$ port wine solution. Other determinations were then made, using twenty-five cc. of acid.

Phosphorus present, 1.63 per cent.

Phosphomolybdate taken.	Fifteen cc. sulphuric acid. Phosphorus found.	Twenty-five cc. sulphuric acid. Phosphorus found.
Gram.	Per cent.	Per cent.
0.0400	1.63	....
0.0380	1.63	....
0.0350	1.62	....
0.0320	1.51	....
0.0300	1.55	1.60
0.0280	1.53	....
0.0250	1.50	1.61
0.0230	1.50	....
0.0230	1.55	1.61
0.0200	1.48	1.51
0.0200	1.55	1.55
0.0180	1.47	1.55
0.0180	1.48	....
0.0150	1.46	1.55
0.0150	....	1.55
0.0160	....	1.54
0.0140	....	1.56
0.0130	1.40	1.51
0.0100	1.40	1.51

This shows the necessity for the precaution of using plenty of sulphuric acid for solution of the zinc.

As before pointed out, results by the foregoing procedure, using all precautions, never fail of the theoretical, 1.63 per cent., or a reasonable approximation thereto, except when the amount of phosphomolybdate taken is only 0.0200 gram (equivalent to 0.018 per cent. in all steel determinations) or less, and the error in that case in a steel never amounts to more than 0.001 per cent. with about two grams of steel taken for analysis; and the writer therefore, on the score of accuracy, prefers this method to the reductor method.

A convenience in phosphorus determinations is a Mohr burette for the sulphuric acid, attached to the sulphuric acid bottle by tubing reaching just to the zero mark of the burette according to the well known plan. The bottle should stand high, and the tubing be wide so that too much lung power will not be required to fill the burette. The delivery tube of the burette should also be of a good width, so that the acid may run quickly into the phosphorus solutions. The apparatus is also convenient for Elliott sulphur determinations, using sulphuric acid for acidifying the caustic soda sulphur solution instead of hydrochloric acid.

There is some difference of opinion among chemists as to the advisability of using sugar for reducing the manganese precipitate formed by the addition of permanganate to the boiling nitric acid solution of the steel. Sugar was originally recommended by Dr. Drown, but Mr. Clemens Jones, obtaining varying results which he attributed to its use, substituted ferrous sulphate with very satisfactory results. Dr. Dudley also states that in using sugar a different result is obtained than when ferrous sulphate is used. On the other hand, Handy and others have claimed that sugar has no harmful effect. The following tests were made by the writer:

No.	Using ferrous sulphate. Phosphorus. Per cent.	Using sugar. Phosphorus. Per cent.
Steel 618	0.017	0.018
" 620	0.018	0.018
Gray pig iron	0.719	0.720
Test bar	0.016	0.016
Steel 684	0.049	0.049
Phosphate solution	0.123	0.121

These results were considered sufficient evidence that sugar does not interfere with the precipitation of the phosphorus. Its use is more advantageous in several respects: it is cheaper than ferrous sulphate; less of it is required; it may be added to the boiling solution without fear of the solution boiling over; and it never contains phosphorus.

The merest pinch of sugar will suffice to reduce a very abundant precipitate of manganese peroxide if the boiling be continued for some time after its addition to the liquid.

For the filtration of the yellow phosphomolybdate precipitate with the aid of the pump, it is the writer's experience that nothing succeeds so well as two seven cm. Schleicher & Schüll No. 579 filter papers, folded and placed in the funnel together. The filtration may be made very rapidly, yet without any of the precipitate going through the paper.

After the solution of the yellow precipitate on the filter paper in ammonia and washing, the same filter may be used (without removal from the funnel) for another phosphomolybdate filtration, and so on for a number of consecutive determinations.

No. 579 is a very loose and porous paper. No. 589 *black ribbon* also serves.

SOME NEW COMPOUNDS OF THALLIUM.

BY L. M. DENNIS AND MARTHA DOAN, with Crystallographic Notes, by A. C. Gill.

Received September 4, 1896.

THALLOUS TRINITRIDE, TlN_3.

WHEN a concentrated solution of potassium trinitride containing a little free hydronitric acid is added to a solution of thallous sulphate, a white, finely crystalline precipitate is formed. This compound is soluble in hot water, and when recrystallized from a hot aqueous solution, it separates in orthorhombic needles of a light straw color.

The thallium in this salt was determined volumetrically by means of a standard solution of potassium permanganate, according to the method of Willm.[1]

In the case of the hydronitric acid, a volumetric method also was first attempted. A weighed portion of the salt was dissolved in water and placed in a Hempel distilling bulb, which was connected by fused joints to a condenser. A separatory funnel was inserted in the neck of the distilling bulb. The hydronitric acid was set free by the addition of an excess of dilute sulphuric acid and was distilled into an Erlenmeyer flask containing a known amount of ammonia, the excess of ammonia being then deter-

[1] *Ann. chim. phys.*, (4), 5, 79.