diameter, slightly contracted at one end, which has a rim over which filter paper and cheese cloth can be tied.

Other apparatus as for available and total phosphoric acid determinations.

Manipulation : Two grams of the substance to be examined are transferred to the extraction tube and washed with from 100 to 225 cc. of hot water, depending upon whether or not water soluble phosphoric acid is to be determined. Dry thoroughly, remove substance carefully, using spatula, brush, and rubber tipped glass rod, and transfer to a separating tube. Add fifteen to twenty cc. of the separating solution, shake thoroughly and wash down the sides of the tube with a jet of the solution. After standing five minutes tap the lower part or bucket smartly with the finger, to release any light portion carried down with the heavy, and stir up the matter on top with a jet of solution.

Let stand until the solution is clear, or for one hour, clamp the rubber tube, place a beaker under the bucket, which is carefully removed, the fingers being encased in rubber finger tips. Filter the solution back into the supply flask, wash thoroughly, saving the first washings for evaporation to a specific gravity of 2.26 again, and treat for insoluble phosphoric acid in the usual way. The light portion is treated in a similar manner. If desired, the heavy and light portions can be treated as for total phosphoric acid, thus determining all of the phosphoric acid derived from inorganic and organic sources respectively, except the water soluble.

MIDDLETOWN, CONN.

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.[1]

BY GEORGE AUCHY.

Received April 16, 1896.

VOLHARD'S method of determining manganese is generally considered a very accurate one ; nevertheless, that the

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[1] In this Journal, 18, 406, I omitted to state a precaution used, in the manner of performing Drown's sulphur method there described. The solution from the Troilius' bulb is heated to boiling (preferably with the previous addition of permanganate solution) before filtering into it the hydrochloric acid solution from the graphitic residue. This is to oxidize any sulphur that may be present as sodium sulphide.

accuracy of the process is strictly dependent upon certain conditions and precautions not pointed out by the author, and not generally recognized (so far as the writer is aware) seems proved by the experience with the method and with Stone's modification of it, which follows :

STONE'S MODIFICATION.

Mr. Geo. C. Stone makes a very considerable saving in time by omitting the evaporation with sulphuric acid, and precipitating the iron immediately with zinc oxid as soon as solution of the drillings in nitric acid is effected.[1] But in Volhard's original article, as also in Blair's Chemical Analysis of Iron, it is directed to destroy the carbonaceous matter by evaporation to dryness and strongly heating, or by evaporation with sulphuric acid till fumes of the latter come off, and as previous to the appearance of Mr. Stone's paper the writer, on testing this point by dissolving in sulphuric acid with enough nitric added to oxidize the iron and help effect the solution of the drillings and omitting the evaporation, had obtained results several hundredths higher (although Volhard's objection to organic matter is that it hinders the balling together of the manganese dioxide in titration) than those obtained from the same samples by the regular process, it was judged that this precaution was not a useless one ; and after reading Mr. Stone's article it was therefore considered well, as a precaution, to test his process also in this particular, and for that purpose the following determinations were made :

TABLE I.

No.	Carbon. Per cent.	Volhard's method. Per cent.	Stone's modification. Per cent.
476	0.585	0.46	0.53
495	0.80	0.57	0.65
503	0.228	0.423	0.45
505	0.225	0.49	0.52
483	0.17	0.43	0.51
486	0.185	0.54	0.61
507	0.315	0.44	0.44

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[1] This Journal, 18, 228. Mr. Stone finds that hydrochloric acid solution also works well.

The results of Stone's method were very considerably higher than those by the regular method, except in the case of 507. But in the case of 507 it was noted that in making the precipitation of the iron by the zinc oxide a large excess had been accidentally used, while in all the other determinations the zinc oxide had been added in amount sufficient to precipitate the iron merely; and it was therefore thought advisable to see whether the considerable differences in the results by the two method's—Volhard's and Stone's—was not due to this fact (insufficient neutralization in the latter) before attributing it to the organic matter undestroyed in Stone's method. The above determinations were therefore repeated, using in each case not only enough zinc oxide to coagulate the solution and precipitate the iron as directed, but also enough in excess of this amount to turn the brownish red color of the iron precipitate to a light brown. The results follow:

TABLE II.

No.	Carbon. Per cent.	Volhard. Per cent.	Stone. Zinc oxide to coagulation. Per cent.	Stone. Zinc oxide in large excess. Per cent.
503	0.228	0.423	0.45	0.45
505	0.225	0.49	0.52	0.51
483	0.17	0.43	0.51	0.45
483	0.17	0.43	0.51	0.45
486	0.185	0.55	0.61	0.58
486	0.185	0.54	0.61	0.58
476	0.585	0.46	0.53	0.47
495	0.80	0.57	0.65	0.60
471	0.105	0.38	....	0.40
480	0.10	0.35	....	0.36
493	0.57	0.46	....	0.47
507	0.315	0.435	....	0.44
153	0.50	0.64	....	0.70
153	0.50	0.64	....	0.67
153	0.50	0.64	....	0.69
155	0.40	0.56	....	0.56

These results show that when the zinc oxide is added merely to coagulation and precipitation of the iron, leaving the solution probably faintly acid, the manganese is afterward precipitated, not according to the theoretical formula, but with result too high;

and that to insure the correct precipitation of the manganese it is necessary to add the zinc oxide in large excess, so that the solution is thoroughly neutralized when titrated.

It will, however, be noted that with this precaution, observed results in the table are nevertheless a few hundredths per cent. higher than by Volhard's method.[1] Is this difference due to the undestroyed carbonaceous matter? It was thought probable, but to make sure, some of the tests were repeated with oxidation of the carbonaceous matter by addition of lead dioxide to the boiling nitric acid solution of the drillings (the excess destroyed by ferrous sulphate and the excess of the latter oxidized by continued boiling of the nitric acid solution).[2] These results should be lower if carbonaceous matter has any influence. They were not lower, as the following table shows, and hence it is indicated that carbonaceous matter does not interfere. It is true that in one case (483) the result obtained by oxidation of the carbonaceous matter is lower, but the reason for this will appear later on.

TABLE III.

No.	Carbon. Per cent.	Stone. With carbon not oxidized. Per cent.	Stone. With carbon oxidized. Per cent.
480	0.10	0.36	0.37
507	0.315	0.44	0.44
155	0.40	0.56	0.55
155	0.40	0.56	0.57
155	0.40	0.56	0.56
155	0.40	0.56	0.56
153	0.50	0.70	0.68
483	0.17	0.45	0.41

Since the slightly high results obtained by Stone's method, in Table II., are not due to the undestroyed carbonaceous matter, they must be due to the fact of titration in nitric acid solution. The following determinations of manganese in solutions containing no organic matter, and in which the amount of mangan-

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[1] It was later seen that the accuracy of the regular Volhard process was also dependent upon certain conditions; and the results by this method, given in these two tables, are the corrected results obtained later by checking with the color method according to Table VI. So that in Tables I. and II. the comparison is really with the color method rather than with Volhard's method. As explained under Table VI., there was not enough left of the samples for gravimetric tests. For a comparison of Stone's method with the gravimetric see Table XI.

[2] The lead dioxide and the ferrous sulphate used were tested for manganese.

ese was known (made by taking definite amounts of standard permanganate solution) are confirmatory of this conclusion :

TABLE IV.

No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.41	8	0.40	0.42
2	0.40	0.41	9	0.80	0.81
3	0.40	0.41	10	0.80	0.82
4	0.40	0.41	11	1.20	1.24
5	0.40	0.41	11	1.20	1.22
6	0.40	0.41	13	0.80	0.81
7	0.40	0.42	14	1.20	1.22

Here, then, is a second precaution to be observed in Stone's method : a correction of the result by one or two hundredths per cent. must in each case be made. But still other precautions are necessary, as will appear.

VOLHARD'S METHOD.

The fact brought out by working upon Stone's method, that titration in faintly acid (nitric) solution gives too high results led to the suspicion that the same was also true of Volhard's regular method (sulphuric acid solution). The following tests were made :

TABLE V.

No.	Volhard. Zinc oxide added to coagulation.	Volhard. Zinc oxide in large excess.
490	0.49	0.39
490	0.49	0.39
490	0.49	0.39
490	0.49	0.49
476	0.51	0.46
507	0.49	0.44
483	0.45	0.41
503	0.45	0.41
471	0.41	0.38
289	0.42	0.40
289	0.42	0.40
493	0.51	0.44
505	0.50	0.46
155	0.58	0.49
155	0.58	0.56
289	0.42	0.41
153	0.66	0.64

Results of the first column were obtained by adding zinc oxide till the solution stiffened and the iron all precipitated. In the second column of determinations the zinc oxide was added in sufficient excess of this amount to make the color of the precipitated iron a light brown. The differences in the results were supposed to be due to this fact already noted in considering Stone's method—that titration in slightly acid solutions gives too high results. But a suspicion arose that these differences might, in part at least, be due to manganese being mechanically carried down with the iron when the large excess of zinc oxide was used. The obvious test of this would have been to make gravimetric determinations in the samples used in the last table. But, unfortunately, there remained but very little drillings of each of the samples. So the next best thing was done, and a standard manganese sample was prepared, and the determinations of these samples of the last table made by the color method: in each case making a number of tests and taking the average. Results:

TABLE VI.

No.	Volhard. Zinc oxide to coagulation.	Volhard. Zinc oxide in large excess.	Color method.
490	0.49	0.39	0.48
507	0.49	0.44	0.435
483	0.45	0.41	0.43
503	0.45	0.41	0.423
471	0.41	0.38	0.38
289	0.42	0.40	0.40
492	0.51	0.44	0.46
503	0.50	0.46	0.49
155	0.58	0.49	0.56

Showing that when the neutralization with zinc oxide is carried only to the point of precipitating the iron the result will invariably be from 0.01 per cent. to 0.05 per cent. too high; while on the other hand, if the zinc oxide be added in excess of this amount, the result *may* be too low, and very much too low from the precipitation of manganese with the iron. These points would have been more certainly and satisfactorily proved, however, had the comparison of the Volhard results been made directly with results by the gravimetric process instead of by the color test. In the following table such comparisons with the gravimetric method—in a new lot of steels—are made, and confirm the conclusions drawn from the preceding table. In the second column of tests, the neutralization was performed in a way not to precipitate the manganese. In the third column of tests, neutralization was purposely performed in a way most favorable to the precipitation of manganese with the iron.

TABLE VII.

No.	Zinc oxide to coagulation. Per cent.	Excess of zinc oxide. The excess added after filtration of ferric oxide. Per cent.	Excess of zinc oxide. Added suddenly to the iron solution. Per cent.	Gravimetric method. Per cent.	Color method. Per cent.
451	0.56	0.51	0.51	0.52 (acetate)	0.53
452	0.46	0.44	0.44	0.43 "	0.435
453	0.46	0.46	0.37	....	0.425
454	0.47	0.47	0.44	0.46 (Ford)	0.45
493	0.51	0.46	0.44	....	0.46
456	0.45	0.41	....	0.41 (Ford)	0.43
466	0.54	0.49	....	0.485 "	0.49
481	0.48	0.45	....	0.455 "	0.46
153	0.66	0.64	....	....	0.64
000	1.30	....	....	1.25[1]	....

Insufficient neutralization gives high results. Complete neutralization *suddenly*, gives low results. Here then is the explanation for the low result of Table III (483); the ferric oxide precipitate had carried down some of the manganese.

The remedy is obvious. It is to carefully avoid an excess of zinc oxide at the time of precipitating the iron; adding the necessary excess to the aliquot part of the filtrate from the ferric oxide, taken for titration—filtering off the undissolved zinc oxide before titrating. But this procedure involves considerable extra work. And it does not seem necessary, if certain precautions be taken, to filter off the ferric oxide before adding the excess of zinc oxide. For it is reasonable to suppose that it is the *sudden* addition of the zinc oxide in excess to the rather concentrated solution that carries down the manganese. If the iron be first precipitated carefully by the gradual addition of zinc oxide, avoiding an excess, we have seen that no manga-

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[1] Made by Williams, of Boston.

nese is carried down. If now, the solution be diluted, mixed, and the ferric oxide be allowed time to begin to settle, there seems no reason why the further addition of an excess of zinc oxide should then precipitate manganese. That it does not is evidenced by the preceding table, second column of results, last four results, which were obtained in this way. Also all of the determinations by Stone's modification in Table XI.

In the determination of the results of the third column of results in the preceding table, pains were taken to add the excess of zinc oxide as suddenly as possible; nevertheless, only three out of the five results are low, showing (as also do the results of Table VI.) that manganese is not invariably carried down by such a procedure. In Stone's modification the tendency to a precipitation of manganese with the iron seems less; for of the numerous results by that method (obtained before the necessity of any precaution in precipitating the ferric oxide was known) only one is low. But in both methods the neglect of the precaution to *thoroughly* neutralize with zinc oxide almost invariably gives results more or less above the truth.

Taught suspicion by the experience thus far had, it was resolved to test every step in the method; and the following determinations were made to see if the temperature of the liquid at the time of neutralization with zinc oxide had any influence upon the result:

TABLE VIII.

Solution heated to boiling with the zinc oxide.			Zinc oxide to cold solution.		
No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.49	1	0.40	0.40
2	0.40	0.44	2	0.40	0.40
3	0.40	0.43	3	0.40	0.40
4	0.40	0.47	4	0.40	0.40
5	0.40	0.42	5	0.40	0.40
6	0.40	0.41	6	0.40	0.39
Solution merely warm.			7	0.40	0.40
1	1.20	1.22	8	0.40	0.41
2	0.80	0.83	9	0.40	0.40
			10	0.80	0.80
			11	1.20	1.20

These results show that neutralization must be performed in the cold. The writer had always practiced this precaution, though for no well defined reason.

The second series of results in the table also show that there is no tendency to slightly high results, as is the case when titration is done in nitric acid solution (Stone's method).

Volhard, in his article, states that the precipitated manganese dioxide is mixed with protoxide unless some metallic base like zinc oxide, lime, magnesia, etc., be present; and, therefore, in the following experiments on this point it was expected that the results would be poor, since the amount of zinc oxide present was purposely kept as low as possible by making the neutralization first with sodium carbonate, and then cautiously adding sulphuric acid till slightly acid, the slight excess of acid being then neutralized with zinc oxide.

TABLE IX.

No.	Taken. Per cent.	Found. Per cent.	No.	Taken. Per cent.	Found. Per cent.
1	0.40	0.41	4	0.40	0.41
2	0.40	0.42	5	0.40	0.42
3	0.40	0.40			

These results seem to show that this is not a very important source of error. In Särnström's method the point is entirely disregarded.

Five determinations made with five cc. free sulphuric acid (two to one) at time of neutralization with zinc oxide give, instead of the theoretical 0.40 per cent. taken, respectively 0.40 per cent., 0.42 per cent., 0.41 per cent., 0.41 per cent., 0.41 per cent.

With six cc. free acid, 0.40 per cent., 0.41 per cent.

With eight cc. free acid, the results of Table VIII.

SÄRNSTRÖM'S METHOD.

Messrs. Mixer and DuBois recommend this method for iron ores,[1] and give results showing its accuracy. In this method zinc oxide is not used, the neutralization (hydrochloric acid

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[1] This Journal, 18, 385.

solution) being effected entirely by sodium carbonate, with care not to add it in greater amount than necessary to precipitate the iron, and the subsequent titration is done without filtering off the ferric oxide thus precipitated. This manner of neutralization leaves the solution not thoroughly neutralized, and from the foregoing results of this article we should expect high results from Särnström's method. The results given by Messrs. Mixer and DuBois are, however, excellent results; and this indicates either that neutralization with sodium carbonate in hot hydrochloric acid solution is not attended with the same phenomena as neutralization with zinc oxide in nitric and sulphuric solutions, or that in the former process there is a greater tendency of the manganese to precipitate with the iron, and that the error from this source counterbalances the error from titrating in faintly acid and hot solution. But the uniform excellence of the results given by Messrs. Mixer and DuBois points to the former as the more likely supposition. The method was briefly tested by taking standard manganese solution. Instead of 0.40 per cent. manganese taken in one case, 0.44 per cent., and in another 0.38 per cent. was obtained. But the test was not a fair one as there was no iron present to give the exact point of neutralization as obtained in the regular working of this method. Ferric chloride should have been added, but none was at hand, and the writer postponed further examination of the method for the reason that (as explained by Messrs. Mixer and DuBois) it is not well adapted to the analysis of steel.

COLOR METHOD.

The color method has no kinship to Volhard's, and its consideration is therefore hardly relevant here. But, nevertheless, as it was found necessary in the course of this work to make determinations by this method for comparison with others obtained by Volhard's method in samples almost used up, it might perhaps be just as well to give these color results in detail, as showing the limits of error in the process when performed by one not an expert in its use.

TABLE X.

No.	First reading. Per cent.	Second reading at a higher dilution. Per cent.		Volhard or gravimetric method. Per cent.	
289	0.40	0.40	0.40	0.40	Volhard.
	0.395	0.39			
	0.40	....			
153	0.63	0.64	0.64	0.64	Volhard.
	0.61	....			
	0.639	0.65			
503	0.552	0.547	0.56	0.56	Stone.
	0.564	0.560			
	0.572	0.586			
	0.543	0.555			
503	0.43	....	0.423	0.41	Volhard.
	0.426	0.416			
	0.42	0.425			
	0.42	0.42			
505	0.495	0.49	0.49	0.49	Stone.
	0.49	0.48			
	0.485	0.485			
	0.495	0.495			
483	0.44	0.425	0.43		
	0.425	0.425			
486	0.53	0.534	0.54		
	0.54	0.546			
471	0.38	0.37	0.38	0.38	Stone.
	0.39	....			
490	0.48	0.48	0.48		
	0.48	0.486			
493	0.438	0.445	0.46	0.46	Volhard.
	0.47	0.466			
	0.468	0.47			
507	0.43	....	0.435	0.42	Stone.
	0.43	0.44			
466	0.488	0.472	0.49	0.485	Gravimetric.
	0.497	0.498			
481	0.49	0.475	0.469	0.455	Gravimetric.
	0.50	0.49			
	0.455	0.454			
	0.47	0.46			
	0.446	0.446			
	0.476	0.47			
453	0.43	0.426	0.425	0.425	Stone.
	0.416	0.425			
456	0.449	0.446	0.43	0.41	Gravimetric.
	0.427	....			
	0.417	0.42			
	0.416	0.428			
	0.417	0.414			
451	0.545	0.56	0.53	0.52	Gravimetrtc.
	0.53	0.53			
	0.54	0.54			
	0.52	0.52			
	0.52	0.525			
	0.537	0.545			
	0.535	0.531			

The results in the table by Volhard's and by Stone's method were obtained by an observance of precautions given—correction of 0.02 per cent. in results by the latter method, thorough neutralization by zinc oxide, etc.

It will be seen that color method results are quite accurate if a number of color comparisons be made and the average taken. But if only one test be made the variation may occasionally be 0.02 to 0.03 per cent. But in these determinations the boiling was all done over the naked flame. Closer results can perhaps be had by using the calcium chloride bath for this purpose, as directed in Blair's Chemical Analysis of Iron.

RECAPITULATION.

The sources of error, then, in Volhard's process, as indicated by the foregoing experiments, are:

1. The incomplete neutralization by zinc oxide, giving usually high results.
2. The too sudden addition of the necessary excess of zinc oxide, giving frequently low results.
3. The titration in nitric acid solution giving results 0.01 or 0.02 per cent. too high.
4. Neutralization by zinc oxide in hot solution, giving high results.

With regard to the first of these sources of error it may be remarked that Volhard recommends slightly acidifying with nitric acid before titration—to oxidize organic matter. But whatever organic matter may be present capable of being oxidized by nitric acid has already been oxidized, and the organic matter and proto salts present in the sodium carbonate and zinc oxide used for neutralization is best determined by a blank or dummy test, or better by performing the process with a convenient measured amount of standard permanganate decomposed by hydrochloric acid. Besides the error from titrating in faintly acid solution, a further objection to acidifying with nitric acid is that the manganese dioxide precipitated by titration collects as a film on the glass and obscures the end reaction.

Stone's modification is much easier and quicker than the regular Volhard method; not only because the evaporation to dryness with sulphuric acid is dispensed with, but also, as Mr. Stone points out, because in nitric acid solution the precipitated ferric oxide settles so readily and completely that the filtration from it may be omitted, the clear liquid being decanted from the precipitate. In sulphuric acid solution the precipitated ferric oxide does not settle readily enough for this, and thus considerable time is taken up in making folded filters, and the filter paper used adds appreciably to the expense of the method.

Mr. Stone performs the neutralization entirely with commercial zinc oxide, and this is doubtless the reason that his results have always been satisfactory, and he has noticed no necessity for the precaution of thorough neutralization; for in neutralizing altogether with zinc oxide, in the hurry of every day work one would naturally get a large or a considerable excess of it used, even if not recognizing the necessity for such an excess. And as to the precipitation of manganese with the iron, the work in this article would seem to show that to be an exceptional occurrence with nitric acid solution, although of frequent occurrence in sulphuric acid solution if caution be not used in the neutralization. But as regards neutralization, the writer considers it more advantageous to use sodium carbonate, or common sal soda first, finishing up with zinc oxide emulsion, for sal soda is much cheaper than commercial zinc oxide. But, as before mentioned, the manganese, organic matter, and proto salts in these reagents, if any be present, must be allowed for.

Mr. Stone takes 100 cc. for titration. But 250 cc. is perhaps preferable on the score of greater accuracy. The writer finds it convenient to use permanganate of strength exactly 0.0056, taking always three and three-tenths grams of the drillings for analysis. The reading of the scale on the burette then at once gives the percentages of manganese without calculation, except a division by ten.

For the convenience of those unfamiliar with the process details briefly follow, with the precautions found to be necessary in this article printed in italics. Three and three-tenths grams of drillings. Dissolve in fifty cc. nitric acid, sp. gr. 1.20. Wash into a 500 cc. measuring flask. Add about two-thirds of the amount of sal soda solution necessary to a complete neutralization. *If not cold, cool.* Add zinc oxide emulsion till solution stiffens, *avoiding an excess.* Dilute to about three-fourths of the capacity of the flask, mix and let stand till the ferric oxide begins to settle. See that the solution is colorless. *Add considerable excess of zinc oxide emulsion.* Mix. Dilute to mark. Insert stopper. Mix. Transfer to dry beaker. Mix again. Let settle, and pour off 250 cc. Titrate in 500 cc. Erlenmeyer flask, (first heating to boiling) with permanganate of strength 0.0056. Make the necessary deduction for impurities in the sal soda and zinc oxide. Divide the number of cubic centimeters permanganate taken by ten. *Deduct 0.02 per cent.*

Following are some comparisons of results by this method with results by Volhard's method, gravimetric method, and color method:

TABLE XI.

No.	Volhard with all precautions. Per cent.	Stone with all precautions. Per cent.	Gravimetric. Per cent.	Color. Per cent.
1451	0.51	0.51	0.52	0.53
452	0.44	0.42	0.43	0.435
453	0.46	0.42 0.43	....	0.425
453	0.47	0.45	0.46	0.45
493	0.46	0.47	....	0.46
466	0.41	0.41	0.41	0.43
466	0.49	0.49	0.485	0.49
481	0.45	0.46	0.455	0.469
153	0.64	0.65	....	0.64

A SIMPLE FORM OF GAS REGULATOR.[1]

BY LUDWIG SAARBACH.

Received April 17, 1896.

A GLASS tube, one end of which is blown out to a bulb is bent around twice, as indicated in Fig. 1, and is provided with a side tube *T*. Some mercury is poured into it, which cuts off a volume of air in bulb *A*. The smaller tube *I* fitting loosely in the wider tube, is connected with the latter by a piece of rubber tubing, which at the same time allows an up and down

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[1] Read before the New York Section, April 10th, 1896.