

- (a) with one per cent. nitric acid, dry and weigh, or
- (b) with one per cent. nitric acid and $\frac{1}{10}$ per cent. potassium nitrate, dissolve and titrate (Handy's method).

The greater part of the analytical work of this paper has been done by my assistant Mr. Geo. O. Loeffler.

METHODS USED.

For Steel and Pig-iron.—The method used in all analyses of steel and pig-iron, was the one published by the author in 1892 (*Trans. Engineer's Society of Western Pennsylvania* March, 1892, and *J. Anal. Appl. Chem.*, April, 1892).

For Ferromanganese.—Two grams, dissolved in nitric acid, (1.42), and the solution evaporated to dryness. The residue, having been redissolved in hydrochloric acid, (1.20) the solution was diluted and filtered. The filtrate was treated with ammonium hydroxide till ammoniacal, then acidified with nitric acid, heated to 85° C. and precipitated with fifty cc. of molybdate solution.

For Iron and Manganese Ores.—Two grams dissolved in aqua regia (five per cent. HNO_3 (1.42) and ninety-five per cent. HCl (1.20), and the solution evaporated to dryness. Subsequent procedure was as described above for ferromanganese after the evaporation. Phosphorus, in "insoluble residues" was separated and determined.

Arsenic was added as dry As_2O_3 to the samples when weighed out. The reagents used in the analysis oxidized it to arsenic oxide.

NOTES AND QUERIES ON DR. DUDLEY'S METHOD OF DETERMINING PHOSPHORUS IN STEEL.

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THE object of the work outlined in this paper was to ascertain the accuracy of the method proposed by Dr. Dudley for the volumetric analysis of phosphorus in steel, described in *J. Am. Chem. Soc.*, Sept., 1893, p. 519, and to determine if a separation of phosphorus could be made in the presence of arsenic with a sufficient degree of accuracy for commercial purposes

by this method or any modification of it.

Our first undertaking was to ascertain if the new ratio between phosphorus and molybdic acid in the yellow precipitate of 1.90, brought forward by Dr. Dudley, was correct. The commonly accepted factor as found by Emmerton and others is 1.794, *Trans. A. I. M. E.*, **15**, 93, R. Finkener, *Ber. d. chem. Ges.*, **11**, 1638, Henry Pemberton, *Chem. News*, **46**, 4, Von der Pfordten, *Ztschr. anal. Chem.*, **23**, 422, and very recent work by H. C. Babbitt, *J. Anal. Appl. Chem.*, **7**, 165, has confirmed this ratio. However, as Dr. Dudley used an entirely different method for determining this ratio, we have followed as nearly as possible his work as outlined in the *American Engineer and Railroad Journal*, Jan. 1893, p. 18, but have been wholly unable to obtain his figure.

Determination of the Ratio between Phosphorus and Molybdic Acid in the Yellow Precipitate.—Four samples of steel of very different carbon composition were taken, and the phosphorus determined both gravimetrically and volumetrically in each, and from the figures obtained, the ratio between the phosphorus and the molybdic acid in the yellow precipitate, formed in the volumetric analysis under the conditions used, was computed. The complete analyses of the steel used in this and subsequent investigations are as follows:

	Carbon, per cent.	Manganese, per cent.	Silicon, per cent.	Gravimetric phosphorus, per cent.	Sulphur, per cent.
No. 27....	0.188	0.321	0.020	0.110	0.052
No. 789....	0.997	0.427	0.226	0.021	0.024
No. 344....	0.588	1.295	0.079	0.065	0.107
No. 65....	0.166	0.577	0.072	0.012	0.025

For our gravimetric determination we used the combination method as described by Dr. Dudley. The acetate method was followed up to the point of obtaining the basic acetate precipitate, at which stage enough bromine water was added to oxidize fully one-half a gram of iron, and the solution boiled. It was then cooled down and the acetate precipitation made exactly as described in Chemical Analysis of Iron, by A. A. Blair. This precipitate was dissolved in hydrochloric acid, and all traces of iron washed from the paper. After expelling the hydrochloric acid from the filtrate by repeated evaporations with nitric acid, seventy-five cc. of nitric acid 1.135 sp. gr. were added, the solu-

tion boiled, oxidized with potassium permanganate, and reduced with ferrous sulphate, as described in Dr. Dudley's routine method. The solution at 85°C. was then treated with seventy-five cc. of molybdic acid at 27°C. , the yellow precipitate shaken down, filtered and washed free of molybdic acid. We test for the presence of molybdic acid as follows: About four cc. of the acid wash water are caught in a test tube as they run through the filter, and treated with a few drops of dilute ammonium sulphide. The least presence of molybdic acid will cause the liquid to darken slightly. The cloud of sulphur produced by the addition of ammonium sulphide to the acid solution does not interfere in any way with the delicacy of the test. We have found this test far more sensitive than the one used by Dr. Dudley, who allows the acid wash water to drop into a dilute solution of ammonium sulphide, the test thus being in the alkaline solution. We have frequently found yellow precipitates which according to the alkaline solution test were thoroughly washed, yet with the acid test show unmistakable signs of molybdic acid which required one or two more washings to remove. The yellow precipitate was then dissolved in ammonia and saturated while warm with hydrogen sulphide, and the red solution of molybdenum sulphide slightly acidified with hydrochloric acid. The precipitate of molybdenum sulphide was allowed to settle, then filtered off rapidly on a large folded filter, avoiding contact with the air as much as possible, and washed thoroughly with strong hydrogen sulphide water containing a little hydrochloric acid. The large filtrate was then evaporated, and on boiling, it was invariably found that a small amount of molybdenum sulphide separated out. This was filtered off and the resulting filtrate concentrated to a bulk of about four cc. The phosphorus was then precipitated with from five to eight cc. of magnesia mixture and a small amount of ammonium hydroxide, the cold solution being vigorously stirred until precipitation began, when ammonium hydroxide amounting to one-third of the bulk of the solution was added, and the analysis allowed to stand for twelve hours. The precipitate was then filtered off, washed with ammonium nitrate until free from chlorine, and ignited. This precipitate was invariably contaminated with molybdic acid. It

was purified by dissolving in hot dilute hydrochloric acid, filtering, evaporating the filtrate to a small bulk, and precipitating as before. For our volumetric determination of the phosphorus in these samples we followed the preceding method up to the point of obtaining the ammoniacal solution of the yellow precipitate. This solution was acidified with sulphuric acid, passed through the reductor and titrated with permanganate, one cc. of which equals 0.003350 grams iron, and assuming as Dr. Dudley has, that the ratio between iron and molybdic acid is 90.76, the commonly accepted factor, we obtain the results in the table below.

No.	Permanganate used by volumet- ric method, cubic centimeters.	Phosphorus by gravimetric method, per cent.	Ratio between phosphorus and molybdic acid.	Error in ratio for each 0.001 per cent. error in gravimetric determination.
27....	103.1	0.110	1 : 1.759	0.016
" 789....	19.0	0.021	1 : 1.826	0.087
" 344....	59.4	0.065	1 : 1.813	0.027
" 65....	11.2	0.012	1 : 1.806	0.151

A glance at the ratios obtained between phosphorus and molybdic acid in the above table will show that they are very irregular, but this will be explained by the last column of figures which point out that the gravimetric determinations of phosphorus must be made with absolute accuracy in order to have these ratios agree. The only point we wish to call attention to in the above table of ratios is the fact that they are all much lower than the ratio 1.90 proposed by Dr. Dudley, and obtained by him in a similar manner.

Not satisfied with the above results, we turned our attention to the actual analysis of the yellow precipitate, which was prepared for our investigations as follows: To a solution of ferric nitrate in nitric acid of 1.135 sp. gr., was added a sufficient amount of phosphoric acid to make the solution correspond to that of a steel containing about one per cent. of phosphorus. The yellow precipitate was shaken down from this, exactly in accordance with Dr. Dudley's method of phosphorus analysis. It was washed by decantation with ammonium sulphate, then with water, and finally dried to a constant weight at 130° C. This precipitate was found to be so hygroscopic that it was practically impossible to obtain accurate weights of it for analy-

sis. To avoid this difficulty, after carefully weighing it, the entire precipitate was dissolved in a slight excess of ammonium hydroxide, filtered through a balanced filter paper into a tared 200 cc. flask, the filter being washed with water until the 200 cc. mark was reached. The small amount of insoluble matter on the filter was determined after drying at 100° C., and the weight deducted from the original weight of the yellow precipitate. We now have a known weight of yellow precipitate in a known weight of solution, successive portions of which were weighed out from time to time for the determination of phosphorus and molybdic acid.

Phosphorus in Yellow Precipitate.—This was determined as follows: Accurately weigh off about twenty-five grams of solution, which is equivalent to about one gram of yellow precipitate, add ten cc. of magnesia mixture, stir well until precipitation begins, then add ammonium hydroxide to the amount of about one-third the bulk of the original solution, and allow to stand for several hours. Filter and wash with ammonium nitrate solution until free from chlorine, then ignite while moist. Purify the magnesium pyrophosphate by dissolving in dilute hydrochloric acid, filtering from any insoluble residue, and precipitating as before by the addition of ammonium hydroxide, five cc. of ammonium chloride solution, and five cc. of magnesia mixture. Allow to stand twelve hours, ignite and weigh.

The reagents used were made up as follows:

Ammonium chloride.—One part ammonium chloride to eight parts of water.

Magnesia mixture.—From magnesium chloride as per Chemical Analysis of Iron, p. 58, by A. A. Blair.

Ammonium hydroxide.—0.90 sp. gr.

Ammonium nitrate wash water.—One part ammonium hydroxide 0.90 sp. gr. to three parts water, then add two grams of ammonium nitrate for each 100 cc. of solution.

Molybdic Acid in Yellow Precipitate.—The method used for this determination was as follows: Weigh off accurately an amount of solution equivalent to about 0.25 gram of yellow precipitate, dilute with 150 cc. of water and bring to a boil. Neutralize the boiling solution with acetic acid, and add about five cc. in excess of the neutral point. Add at once twenty-five cc. of lead acetate,

or one cc. for every 0.01 gram of yellow precipitate present in the solution, and allow to digest an hour and a half at nearly a boiling temperature, in order to render the precipitate compact and granular. Filter on a Gooch crucible and wash with hot water about eight times by decantation. After the fifth or sixth washing the filtrate should give no reaction for lead when tested with ammonium sulphide. Dry to a constant weight at 130°C . This gives us the weight of $\text{Pb}_3(\text{PO}_4)_2 + \text{PbMoO}_4$. From the previous determination of phosphorus we now compute the $\text{Pb}_3(\text{PO}_4)_2$, and deduct this weight from that of the mixed precipitates. The difference gives us the weight of PbMoO_4 , which multiplied by the factor 0.39237 equals molybdic acid (MoO_3).

The reagents used were made up as follows:

Lead Acetate.—Sixty grams crystallized salt in two liters of water, to which fifteen cc. of acetic acid were added.

Acetic Acid.—1.04 specific gravity.

Before using the above method for the determination of molybdic acid, we carefully investigated its merits and found it to be thoroughly reliable under all ordinary conditions of precipitation, the acidity, bulk and temperature of the solution having only a slight influence. On attempting to ignite the precipitate, however, as directed in the method as originally published in the *Ber. d. chem. Ges.*, 4, 280, we invariably found a loss varying from 0.2 per cent. to 3.0 per cent., and even more, according to the duration and intensity of ignition. But by drying on a Gooch crucible at 130°C . we obtained very constant results, which we believe to be in every way reliable.

The analysis of the yellow precipitate by the above methods gave us as follows: Phosphorus, 1.648 and 1.644 per cent., an average of 1.646 per cent.

Molybdic acid, 91.61, 91.59, 91.61 and 91.57 per cent., an average of 91.595 per cent. Our ratio between phosphorus and molybdic acid as computed on these analyses is 1.797.

We determined the molybdic acid in the filtrates from the phosphorus determinations and obtained 92.25 and 92.41 per cent. These results are higher than those previously obtained in the separate determinations, but as this difference was not sufficient to change to any extent our ratio we did not investigate the cause.

We now went a step further, in order to prove that the ratio between the phosphorus and molybdic acid in the yellow precipitate actually obtained in a steel analysis, is identically the same as that in the yellow precipitate shaken down from the prepared solution of phosphorus.

We separated a considerable amount of yellow precipitate from a steel containing 0.10 per cent. phosphorus, by Dr. Dudley's method of analysis, and after drying to a constant weight at 130° C. made the determinations of phosphorus and molybdic acid exactly as in the case of the previous precipitate, obtaining the following results: Phosphorus, 1.638 and 1.648 per cent., an average of 1.643 per cent. Molybdic acid, 91.63 and 91.67 per cent., an average of 91.65 per cent.

The ratio between phosphorus and molybdic acid given by these figures is 1.792, thus confirming our previous results and the generally accepted figure of 1.794.

From the work above outlined it would seem evident that the ratio of phosphorus to molybdic acid can be derived much more accurately from the analysis of the yellow precipitate than by the method suggested by Dr. Dudley.

The elaborate investigations of Hundeschagen (*Chem. News*, Oct. 4, 11, 18, 25, and Nov. 1, 1889,) have shown that ammonium phosphomolybdate is far more uniform when prepared under varying conditions than was formerly supposed. If the conditions of precipitation of the yellow precipitate are maintained constant, there is but little doubt as to its uniform composition. The ratio then becomes a question of the accuracy of the determinations of phosphorus and molybdic acid in the yellow precipitate. We have accordingly given the methods used for these determinations as completely as possible, in order to afford an opportunity for criticism and duplication.

Ratio between Iron and Molybdic Acid.—The ratio between phosphorus and molybdic acid being established, we then took up the ratio between iron and molybdic acid, as the investigations of Mr. Babbitt, *J. Anal. Appl. Chem.*, **7**, 165, and our own experience had indicated that the commonly accepted ratio, 90.76, is too high where the reductor is used, the reduction being considerably greater than with the ordinary method of reducing with zinc powder and shot.

Our first experiments were on the standardization of a permanganate solution by the ordinary method of dissolving the steel in a flask in an atmosphere of carbon dioxide gas, as compared with the figure obtained when the steel was dissolved in an open beaker and reduced through the reductor. No appreciable difference was found, the reduction being complete in both cases.

We then made a large solution of molybdic acid of such a strength that fifty cc. contained 0.25 gram of the salt. The first experiments with this solution were made after the reductor had been in use some time, and the zinc was packed closely together, so that the solution encountered considerable resistance to its progress, and the acid had some time to act on the zinc, the result being that the reductor became quite hot. Upon cleaning out the reductor and filling with entirely fresh zinc, we were surprised to find our results very appreciably lower, no matter how slowly the solution was passed through the reductor, and only after heating the solution nearly to boiling did we obtain the results in the first case. This demonstrates that care must be taken to have the solutions hot when they are reduced, in order to obtain complete reduction, but with this precaution the results are very uniform, as will be seen from the table following. In each of the following experiments fifty cc. of the above mentioned molybdic acid solution was used.

Experiments with reductor:

RESULTS EXPRESSED IN CUBIC CENTIMETERS OF PERMANGANATE.

REDUCTOR CLOGGED FROM LONG USE.		REDUCTOR CONTAINING FRESH ZINC.		
Five cc. sulphuric acid, cubic centimeters.	Ten cc. sulphuric acid, cubic centimeters.	Five cc. sulphuric acid, cubic centimeters.	Ten cc. sulphuric acid, cubic centimeters.	Five cc. sulphuric acid solution heated to 95° C., cubic centimeters.
....	75.2	74.8	74.6
75.25	75.3	75.0	74.7	75.45
75.35	75.4	74.9	74.7	75.35
75.45	75.3	74.95	74.8	75.35
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Average, 75.35	75.3	74.91	74.70	75.38

Our experience with the reductor has been that in order to secure complete reduction, it is necessary to have the column of zinc of considerable length, and to pass the solution through

very slowly. We would not feel safe in using a column of zinc less than ten inches in length. In reducing a solution which has a bulk of 200 cc. at least two minutes should be allowed for passing through.

Turning now to the reduction of molybdic acid by heating with zinc and sulphuric acid, we found that very different results could be obtained by the various modifications of the method. These methods vary not only in the amounts of zinc and sulphuric acid recommended, but also in the temperature used and the time of heating.

We experimented with the method given in Chemical Analysis of Iron, by A. A. Blair, p. 97. Fifty cc. of our stock molybdate solution reduced in this manner required 73.23 cc. of permanganate.

We then reduced the molybdic acid solution as follows: Fifty cc. of stock molybdic acid were measured off, twenty grams of zinc (and four large shot) were added, together with thirty cc. of ammonia (1:3). This was heated almost to boiling, eighty cc. of hot sulphuric acid (1:4) added, and allowed to reduce for fifteen minutes, keeping the solution at a gentle boil. Fifty cc. of the stock solution reduced in this manner gave as a mean of a number of determinations 74.2 cc. of permanganate.

It will be noticed that there is quite a difference between these results, and also that the highest value obtained by the zinc and sulphuric acid method is considerably lower than that given by the reductor. In some laboratories the zinc and sulphuric acid method of reduction is used with a less amount of zinc, shorter time, and at temperatures which do not reach the boiling point. In such cases the reduction is certainly far from complete.

The mean of four gravimetric determinations upon this same solution show the amount of molybdic acid contained in fifty cc. to be 0.233264 gram. The average number of cubic centimeters of permanganate used in titrating this amount after being passed through the reductor is 75.35, hence one cc. permanganate = 0.003096 molybdic acid. A careful standardization of the permanganate solution against iron gave its value as one cc. = 0.003472 gram iron, hence the ratio between iron and molybdic

acid, when the reduction is made by means of the reductor in our hands gives 89.16 instead of 90.76 as found by Mr. Emmerton. This difference is readily accounted for by the difference in the method of reducing the solutions. Our figure tends to corroborate the work of Mr. Babbitt in this connection although it does not correspond exactly with the one he obtained. From the foregoing work it would seem that the ratio between phosphorus and molybdic acid of 1.794 is correct, but that where the reductor is used 89.16 represents more nearly the correct ratio between iron and molybdic acid, hence our results are computed on this basis.

The Effect of Temperature on the Precipitation of Arsenic.—With the exception of these factors we found no fault with the method given by Dr. Dudley and the uniformity of the results obtained was very gratifying. To divide the errors liable to occur in weighing out the sample, and for convenience in manipulation, we have altered the method slightly in the direction of using a larger sample of steel and smaller bulk of solutions. A large number of determinations have proved that we do not in any way decrease the accuracy of our results by these changes. In detail, the method, as used by us, is as follows: Dissolve 1.5 grams steel in seventy-five cc. nitric acid 1.135 sp. gr. in an eight-ounce Erlenmeyer flask, allow to dissolve on the hot plate and boil hard for about one minute after the steel is in complete solution. Add crystals of potassium permanganate until a permanent purple color is obtained which will remain for at least one-half a minute on boiling. In order to secure such a color, enough permanganate must be added to form a copious dark brown precipitate of manganese dioxide. The crystals of permanganate must be added carefully to prevent the solution from boiling over. Remove the flask from the plate and add ferrous sulphate free from phosphorus, with constant shaking, until the solution clears. Cool to 38° C. and add seventy-five cc. molybdic acid at 27° C. Shake hard for five minutes, filter off the yellow precipitate and wash with ammonium sulphate wash water until the filtrate shows no reaction for molybdic acid when tested as previously described. Dissolve the precipitate in ammonia (1:3), using as little as possible. Wash the paper once with water, and pass the liquid back through the filter and wash

thoroughly. The bulk of this filtrate should not exceed 150 cc. Acidify with five cc. concentrated sulphuric acid, and reduce with the aid of the reductor, passing the liquid slowly through a ten-inch column of zinc. Titrate with potassium permanganate.

Our next step was to ascertain if the method or any modification of it could be used in the presence of arsenic without serious error from that source. Solutions of arsenic were made up by dissolving arsenious oxide in a small amount of a solution of sodium acid carbonate, and diluting with nitric acid 1.135 sp. gr. The strength of these solutions was so adjusted that seventy-five cc. of each would correspond to 0.1, 0.5, and 1 per cent. of arsenic when 1.5 grams of steel are used. Blank experiments were first made with the chemicals to be used, following in every detail the method given. The average of the results obtained are given in the table which follows. We then shook down in the same manner the three arsenic solutions prepared as stated, trying the effect of different temperatures, but were unable to bring down any appreciable amount of arsenic as the table will show.

	Percentage of arsenic added.	Temperature of solution.	Temperature of molybdic acid.	Temperature of the mixture when shaken.	Result in terms of phosphorus, per cent.	Blank exper. on chemicals in terms of phosphorus, per cent.	Arsenic obtained in terms of phosphorus per cent.
Blank exper.	..	85° C.	27° C.	52° C.	0.0006
Blank exper.	..	16°	16°	16°	0.00034
Blank exper. plus arsenic.	1	85	27°	52°	0.0023	0.0017
"	1	16°	16°	16°	0.0010	0.0006
"	5	85°	27°	52°	0.00055	0.0051
"	5	85°	27°	52°	0.0016	0.0010
"	5	27°	27°	27°	0.0017	0.0012
"	5	27°	27°	27°	0.0014	0.0011
"	1	85°	27°	52°	0.0014	0.0011
"	1	16°	16°	16°	0.0017	0.0012
"	1	16°	16°	16°	0.0018	0.0015
"	1	16°	16°	16°	0.0018	0.0015

These tabulated results gave us no little surprise, being so entirely contrary to the behavior usually attributed to arsenic. But we have repeatedly duplicated them, confirming our first results in every case. To investigate the matter still further we made a solution of pure nitrate of iron and phosphoric acid of such a strength that twenty cc. contained approximately 1.5 grams of iron and one-half per cent. of phosphorus. Analysis of

this solution, made as before and shaken down at $85^{\circ}\text{C}.$, gave 0.442 per cent. phosphorus, duplicate 0.446 per cent. On the addition of 0.25 per cent. of arsenic to this solution and shaking down at 85° we obtained 0.484 per cent. phosphorus, duplicate 0.489 per cent., or an increase of 0.4 per cent., due to the arsenic added. We then took the four samples of steel on which our previous work had been done, and to each of these was added 0.1 per cent. of arsenic and the analysis shaken down with the results shown in the following table:

	Arsenic added, per cent.	Temperature of solution.	Temperature of molybdic acid.	Temperature of mixture when shaken.	Phosphorus obtained before arsenic was added.	Phosphorus obtained after arsenic was added.	Arsenic obtained in terms of phosphorus.
Iron salt plus phosphoric acid.	0.25	$85^{\circ}\text{C}.$	$27^{\circ}\text{C}.$	$52^{\circ}\text{C}.$	0.442	0.484	0.042
No. 27.	0.10	"	"	"	0.110	0.119	0.009
" 789.	0.10	"	"	"	0.021	0.022	0.001
" 344.	0.10	"	"	"	0.066	0.067	0.001
" 65.	0.10	"	"	"	0.012	0.012	0.000

As the arsenic in these determinations was precipitated under identically the same conditions as were previously used in our blank experiments, except phosphorus being present, it is reasonable to infer that the action is a mechanical one, the ammonium phosphomolybdate carrying down with it a little of the arsenomolybdate, the amount depending largely upon the size of the precipitate. Our results given above tend to demonstrate this quite conclusively. We repeated the above work using Wood's formula for molybdic acid, shaking for ten minutes instead of five, allowing the precipitate to stand for fifteen minutes before filtering off, to ascertain if any of these variations had any influence on the precipitation of arsenic. We found that they made no appreciable difference in our results. If the method is followed as outlined, and the temperature of the solutions is not higher than that specified, so that the actual temperature at which the shaking takes place does not exceed 49° to $55^{\circ}\text{C}.$, the error will never be appreciable, except in the case of a steel very high in both phosphorus and arsenic. One point, however, we have been unable to check up, and that is if arsenic which has been reduced from the ore with the iron behaves the same as

arsenic artificially introduced. We were wholly unable to obtain a sample of steel containing an appreciable amount of arsenic, upon which to work, and have been obliged to leave this until some future time when we may be fortunate enough to secure the necessary sample.¹ It is conceded by every one that temperature is an all-important factor in the precipitation of phosphorus in the presence of arsenic. We know that above a certain temperature arsenic is sure to come down in greater or less amounts. The question then arises, how high a temperature is necessary for the complete precipitation of phosphorus, or in other words, how low a temperature can we use and feel sure we have precipitated all the phosphorus. Numerous experiments upon various samples of steel at 32° and 55° temperature have shown that the results at 32° C. are slightly lower. This difference does not usually exceed 0.001 per cent. if precautions are taken to thoroughly shake the solution, and to use a paper sufficiently close to hold every trace of the fine precipitate. In view of the fact that the difference between the results obtained at the two different temperatures is so slight, and also that there is danger of contamination in the case of a steel high in both phosphorus and arsenic, we adopted the lower temperature.

It may be asked how do the results obtained by this volumetric method compare with those given by gravimetric methods of wide reputation, such as the acetate method. We regret that we were unable to make acetate determinations of the phosphorus in the four standard samples of steel previously used, but our investigations of the molybdate method proved so much more exhaustive than we had anticipated, that these samples were used up in that work. However, we spent considerable time on a steel which had been examined by a number of well-known chemists. The results obtained by others are as follows:

Acetate method.	Molybdate method.
0.047 per cent. phosphorus.	0.059 per cent. phosphorus.
0.048 " " "	0.050 " " "
0.046 " " "	0.060 " " "
0.050 " " "

¹ Since writing the above we have received, through the kindness of Mr. W. P. Barba, of the Midvale Steel Company, a sample of steel said to contain 0.093 per cent. phosphorus, and approximately 0.12 per cent. arsenic. The average of a number of determinations on this sample, by the above method, gave 0.095 per cent. phosphorus—thus confirming what we had previously observed.

Our results on this sample were 0.048 by the acetate method and 0.055 by the volumetric. By the combination method described above, which seems to exclude many of the chances of error which occur in either the acetate or molybdate method, we found 0.0538 per cent. phosphorus.

It will be noticed that the results obtained by the acetate method are lower than either of the others. This has been our experience repeatedly, when we have compared the three methods, the acetate giving invariably the lowest results.

We will not enter into a discussion in regard to the causes for this as they are many, and this is not the purpose of our paper, but in our opinion the proposed Committee on Standard Methods can do no greater benefit to the iron industry of our country than by a thorough investigation of the methods used for the determination of phosphorus in ores and finished products. From our personal observation we know that frequently injustice is done, and able chemists brought into disrepute, simply because their results have not agreed with those obtained by analytical chemists of wide reputation, whose methods have not told the whole truth.

ON THE QUALITATIVE DETERMINATION OF TANNING MATERIALS.¹

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IT can hardly be said that any systematic attempt has been made to formulate a scheme for distinguishing the various tanning materials by their qualitative reactions, except perhaps a very slight table published by the writer, although, in view of the constantly increasing number of new tanning materials, and especially of new extracts which are offered to tanners, the matter has become one of considerable practical importance. The commercial value of an extract is dependent, not only on the percentage of tanning matter as determined by analysis, but on the nature of the tannin present, which influences the character of the leather produced.

It is, of course obvious, that, failing a clear knowledge of the

¹ Read before the World's Congress of Chemists, August 25, 1893. Proof of this article was kindly read by Professor Henry Trimble.