| Iron added. Grams. | Nickel taken. Gram. | Nickel recovered. Gram. | Gain and loss. + — Gram. | Method. |
|---|---|---|---|---|
| 0.2105 | 0.08892 | 0.08910 | + 0.00018 | Electrolytically. |
| 1.0000 | 0.03430 | 0.03435 | + 0.00005 | " |
| 1.0041 | 0.05298 | 0.05345 | + 0.00047 | " |
| 1.0043 | 0.10824 | 0.10825 | + 0.00001 | " |
| 2.0043 | 0.02690 | 0.02740 | + 0.00050 | " |
| 1.0010 | 0.00100 | 0.00089 | — 0.00011 | Volumetrically. |
| 1.0086 | 0.06578 | 0.06532 | — 0.00046 | " |
| 1.0066 | 0.07582 | 0.07583 | + 0.00001 | " |
| 1.0057 | 0.08017 | 0.08050 | + 0.00033 | " |
| 1.0071 | 0.09389 | 0.09381 | — 0.00008 | " |

ANN ARBOR, MICHIGAN,
December 18, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. VI.]

# THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.[1]

BY W. A. NOYES AND J. S. ROYSE.

Received January 3, 1895.

IN a previous paper[2] one of us, with Mr. E. D. Frohman, showed that in the reduction of molybdic solutions by means of Jones' reductor, the molybdenum is reduced to a form corresponding to the oxide $Mo_2O_3$. We also showed that the reduced solution is very easily oxidized by exposure to the air, and we were led to believe this would account for the difference between the theoretical factor for the calculation of the phosphorus equivalent of a permanganate solution from its iron equivalent, and the empirical factor as given by Dudley and Pease.[3]

In a private communication, however, Dr. Dudley has very kindly called our attention to the fact that he obtained the same results when following the directions for reduction given in our paper as when following the method which he had previously used. As the difference between his results and ours corresponded to only three-tenths or four-tenths cc. of the permanganate solution used, and the results obtained by Mr. Frohman

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[1] Read at the Boston Meeting, December 28, 1894.

[2] This JOURNAL, 16, 553.

[3] This JOURNAL, 16, 230.

were not sufficiently accordant to establish the point in question, it became necessary to repeat that part of the work. Accordingly, the following series of determinations was made, following, as closely as possible, the directions given by Dudley and Pease.[1] The results are given in per cents., on the basis of one gram of steel.[2]

| | Phosphorus present. | Phosphorus found. | |
|---|---|---|---|
| | | By theoretical factor. | By factor of Dudley and Pease. |
| Steel No. 1 | 0.040 | 0.040 | 0.045 |
| " " 1 | 0.040 | 0.0354 | 0.0397 |
| " " 2 | 0.053 | 0.0525 | 0.059 |
| " " 2 | 0.053 | 0.0525 | 0.059 |
| " " 3 | 0.032 | 0.0264 | 0.0296 |
| 5 grams cryst. $FeSO_4$ + 0.0011 gram cryst. $Na_2HPO_4$ | 0.010 | 0.0035 | 0.0039 |
| 5 grams cryst. $FeSO_4$ + 0.0130 gram cryst. $Na_2HPO_4$ | 0.113 | 0.127 | ..... |
| 5 grams cryst. $FeSO_4$ + 0.0097 gram cryst. $Na_2HPO_4$ | 0.084 | 0.091 | ..... |
| 5 grams cryst. $FeSO_4$ + 0.0109 gram cryst. $Na_2HPO_4$ | 0.094 | 0.106 | ..... |
| 1 gram steel No. 3 + 0.0068 gram cryst. $Na_2HPO_4$ | 0.091 | 0.097 | ..... |
| 1 gram steel No. 3 + 0.0026 gram cryst. $Na_2HPO_4$ | 0.055 | 0.054 | 0.0061 |

The first result is evidently wrong for some unknown reason. Omitting this, the results with steels Nos. 1 and 3 show conclusively that the factor of Dudley and Pease is correct for those steels and the statement of our first paper was erroneous. As regards steel No. 2 the case is different. Dudley and Pease explain the higher results obtained with this steel as due to arsenic which it contains. The results of the last determination in the table, and, still more, the results obtained by another method and given below, lead us to believe that this is not the case, but that for a steel containing 0.055 of phosphorus the theoretical factor gives very nearly correct results.

From the examination of the table as a whole it becomes apparent, at once, that, while the factor given by Dudley and Pease gives results nearly or quite correct for steels containing 0.03 to

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[1] *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

[2] This set of determinations was made by W. A. Noyes.

0.04 per cent. of phosphorus, it fails entirely so soon as the amount present is either above or below these limits. The reason is, we believe, apparent. When the amount of phosphorus is less than 0.05 per cent., a part of it escapes precipitation, and hence, a larger factor than the theoretical is required. When the amount of phosphorus is as great as 0.08 per cent. or more, however, the yellow precipitate probably carries down with it at 55° C., some free molybdic anhydride, and even the theoretical factor gives too high results. If we retain the method in its present form, therefore, it will be necessary to use several different empirical factors, or to apply a correction varying with the amount of phosphorus present in the steel under examination. We believe such a course is open to very serious objection and that it should be avoided, if possible. The use of a variable correction implies that the yellow precipitate is not a pure chemical compound, but that it has a variable composition dependent on the amount of phosphorus present. If we admit this, it is evident that the method is not a suitable one on which to base an accurate determination, for a compound or mixture of variable composition is liable to be seriously affected by even slight changes in manipulation, changes which are sure to occur in different hands and different laboratories.

These considerations led us to endeavor to modify the method in such a manner as to secure, if possible, a practically complete precipitation of very small amounts of phosphorous and also to secure the precipitation in the form of a compound of definite composition and independent of the amount of phosphorus present. The considerations which have guided us in the study are as follows: first, the precipitation would be more rapid in a more concentrated solution; second, the precipitation must be at a lower temperature than 55° to prevent the contamination of the precipitate with molybdic anhydride; third, the precipitate is formed more rapidly in a more nearly neutral solution; and fourth, the presence of ammonium nitrate hastens the formation of the precipitate, probably because ammonium enters into its composition.

Without going into the details of unsuccessful experiments, we will give the method which we have found most satisfactory.

We give details for reagents and apparatus, though most of these details are a repetition of those given by Dudley and Pease.

## REAGENTS AND APPARATUS.

*Nitric Acid.*—One part of concentrated acid (1.42) to two parts of water by volume. This gives an acid of sp. gr. 1.18.

*Oxidizing Permanganate Solution.* — Twelve and one-half grams of potassium permanganate in one liter of water.

*Ferrous Sulphate.*—The crystallized non-effloresced salt, *free from phosphorus.*

*Ammonia.*—Concentrated, sp. gr. 0.90; and dilute, sp. gr. 0.96.

*Molybdic Solution.*—Dissolve 100 grams of molybdic anhydride in 400 cc. of ammonia (0.96), filter and pour the solution slowly, with constant stirring, into 1,000 cc. of nitric acid (1.20). Warm to 45°, add one cc. of a ten per cent. solution of crystallized sodium phosphate, stir vigorously, and allow to stand in a warm place over night before using. The addition of the sodium phosphate was suggested by Dr. Dudley and has the two-fold object of precipitating anything liable to contaminate the yellow precipitate and of leaving the solution saturated with the compound which is to be precipitated by it. Our experience leads us to think that the solution keeps better in the dark. It is always safer to filter it immediately before it is used and the solution must, of course, be absolutely clear. If pure, it will be almost or quite colorless, but we have found that a somewhat yellow solution prepared as above, gave us results nearly or quite identical with those obtained with a colorless solution.

*Acid Ammonium Sulphate.*—To one half liter of water add twenty-seven and one-half cc. of ammonia (0.96) and twenty-four cc. of concentrated sulphuric acid and make up to one liter.

*Potassium Permanganate for Titration.*—Dissolve four grams of potassium permanganate in two liters of water, heat nearly to boiling for an hour, allow to settle over night, and filter with the pump, using an asbestos filter prepared after the manner of Gooch on a small perforated porcelain plate placed in the bottom of a large funnel. Use very great care that the solution does not come in contact with india-rubber or any kind of organic matter and keep in a clean glass-stoppered bottle, free from manganese oxides. We find that a solution prepared in this manner keeps perfectly and is not affected by the light.

We prefer to standardize with freshly crystallized and thoroughly air-dried ammonium oxalate dissolved in water with the addition of a little dilute sulphuric acid (instead of considerable concentrated acid as advised by Fresenius) and with ferrous ammonium sulphate freshly crystallized in small crystals from a slightly acid solution, the crystals being thoroughly washed and quickly air-dried in a thin layer, using the factors $\frac{112}{142}$ and $\frac{1}{7}$ respectively to calculate the iron equivalent[1]. The phosphorus equivalent is obtained by multiplying the iron equivalent by $\frac{31}{36\times56} = 0.01538$.

*Jones' Reductor.*—A piece of moderately heavy glass tubing thirty-five cm. long and having an internal diameter of about two cm., is drawn out at one end to pass through the stopper of a filtering flask. In the bottom of the tube is placed a small perforated porcelain plate and on this is prepared an asbestos filter, practically a Gooch filter. This filter should offer enough resistance so that a reduction will occupy two or three minutes. The tube is nearly filled with powdered zinc, which is then washed with dilute sulphuric acid (1:20 by volume). Blank determinations are made as follows: To 180 cc. of water, add twelve cc. of ammonia (0.96) and ten cc. concentrated sulphuric acid. Pass the solution through the reductor and follow with 200 cc. of water, *taking care that no air passes through the reductor*. It is easily shown, qualitatively, that hydrogen peroxide is formed by passing air and water alternately through the reductor. After standing, even for a few minutes, the reductor should be rinsed with dilute sulphuric acid before use. Blank determinations should be made frequently and the amount of

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[1] The method given by Dudley and Pease (This JOURNAL, 15, 521,) has given me practically identical results with the above methods, also piano wire, considering it as pure iron, the impurities in iron, some of them, requiring more permanganate than iron itself. The following results were obtained:

| | |
|---|---|
| Iron wire (Fresenius' method) | 0.003199 |
| Ammonium oxalate | 0.003209 |
| Ferrous ammonium sulphate | 0.003209 |
| Dudley's steel | 0.003179 |
| " " | 0.003205 |
| " " | 0.003208 |

W. A. NOYES.

permanganate required should be subtracted from that found in an analysis. The blanks should not take more than two-tenths to three-tenths cc. of permanganate. Ours are usually less than two-tenths cc. We do not think it advisable to use the same reductor for both iron and molybdenum solutions.

## ANALYTICAL PROCESS.

Weigh two grams of steel[1] to an accuracy of two mgms., put it in a 500 cc. (16 oz.) flask, add fifty cc. of nitric acid (1.18), and warm, only gently, till solution is complete, (our experience leads us to think some phosphorus may escape if the gases in the flask become colorless before solution is complete) ; then boil for one minute, add ten cc. of the permanganate solution (one and one-fourth per cent.), boil till the pink color disappears, add ferrous sulphate carefully, with shaking, till the solution clears, cool to about 50°, add eight cc. ammonia (0.90), insert the stopper, and shake till any precipitate which forms redissolves; cool or warm till the solution is as many degrees above or below 60° as the molybdic solution is below or above 27°, add sixty cc. of molybdic solution, insert the rubber stopper, and shake by hand or with a machine for five minutes; allow to settle for five minutes, filter through a nine cm. filter of rather fine texture, wash with the acid ammonium sulphate solution, putting five or ten cc. at a time into the precipitation flask and pouring from that all around the upper edge of the filter. The filtrate and washings must be absolutely clear. Wash till five cc. of the washings give no brown color with a few drops of dilute hydrogen sulphide water. Pour over the precipitate twelve cc. of ammonia (0.96) diluted to twenty-five cc., allow the solution to run into the precipitation flask, wash with 100 cc. of water, add eighty cc. more of water and ten cc. of concentrated sulphuric acid, pass the solution through the reductor and follow it with 200 cc. of water, *taking care that no air passes through the reductor* during reduction or washing. Titrate the solution, *at once, in the reductor flask.*

With steels high in phosphorus, the ammoniacal solution of the yellow precipitate may be made up to a known volume and an aliquot part taken for reduction.

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[1] Dr. Dudley suggested the use of two grams of steel.

For cast iron low in phosphorus, the method may be carried out exactly as given for steel. The method may also be used without modification other than the use of a larger amount of ammonia for solution of the yellow precipitate and the use of an aliquot part of the solution for reduction, for cast iron high in phosphorus. We prefer, however, in that case, to use one gram of the iron, dissolve, oxidize, clear, and neutralize as usual, using twelve cc. of ammonia. Then the solution is made up to 150 or 250 cc. and ten cc., or more, taken, enough water added to make fifty cc., the solution warmed to 60° and sixty cc. of molybdic solution added. The remainder of the process is as above for steel. The residues insoluble in nitric acid may require examination as usual.

The process as here described has given us the results stated in the table below. No determinations which have been made by this method have been omitted. Steels Nos. 1, 2, and 3 were kindly furnished us by Dr. Dudley, and are the same as those described in this JOURNAL, **16**, 217, and the gravimetric determinations given are the very careful ones reported in that paper. Steel "a" was also furnished us by Dr. Dudley with the statement that it contains, by their determination, 0.016 per cent. phosphorus, and is the lowest they have. Steel C is a tool steel containing, probably, about one per cent. of carbon, and, by our own gravimetric determination by the combined acetate-molybdate-magnesia method[1], using ten grams of the steel, 0.021 per cent. of phosphorus. Steel A is a mild steel containing about 0.17 per cent. carbon and, by the molybdate-magnesia method, using five grams, 0.129 per cent. phosphorus. We do not place as much reliance on this gravimetric determination as on the other.

The gravimetric determinations for the cast iron were made as follows: one gram of the iron was dissolved in fifty cc. of nitric acid (1.18) and treated exactly as in our directions for steel. The ammoniacal solution of the yellow precipitate was made up to 150 cc. and two portions of ten cc. each were taken for reduction. These portions gave determinations 18–21 of the table. The remainder of the ammoniacal solution was concentrated in a platinum dish and then precipitated with magnesia mixture.

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[1] This JOURNAL, 16, 221.

The magnesium pyrophosphate, after weighing, was dissolved in hydrochloric acid and evaporated to separate silica. In the first determination no silica was found; in the second there was an appreciable amount. The gravimetric determinations gave 1.75 and 1.79 per cent. of phosphorus, respectively.

In order to determine if more phosphorus could be obtained by solution in aqua regia, one gram of the iron was dissolved in thirty cc. of a mixture of equal volumes of concentrated nitric and hydrochloric acids; the solution was made up to 150 cc.; ten cc. were placed in a porcelain dish with five cc. of concentrated nitric acid, evaporated to dryness, and heated to 200° for one-half hour, the residue taken up with fifty cc. of nitric acid (1.18), nineteen cc. of ammonia added, and the solution precipitated as usual. This method gave the determinations 22 and 23 of the table. Determinations 24 and 25 of the table were made by the method recommended above for cast iron.

| | | Gravimetric determination. | | Volumetric determination. | |
|---|---|---|---|---|---|
| 1. | Steel No. 1 | 0.040 | per ct. | 0.037 | per ct. |
| 2. | " " 1 | 0.040 | " | 0.040 | " |
| 3. | " " 1 | 0.040 | " | 0.041 | " |
| 4. | " " 1[1] | 0.040 | " | 0.0404 | " |
| 5. | " " 2 | 0.053 | " | 0.0512 | " |
| 6. | " " 2 | 0.053 | " | 0.0548 | " |
| 7. | " " 2 | 0.053 | " | 0.0526 | " |
| 8. | " " 3 | 0.032 | " | 0.0317 | " |
| 9. | " " 3 | 0.032 | " | 0.032 | " |
| 10. | " " "a" | 0.016 | " | 0.0177 | " |
| 11. | " " "a" | 0.016 | " | 0.0174 | " |
| 12. | " " C | 0.021 | " | 0.021 | " |
| 13. | " " A | 0.129 | " | 0.129 | " |
| 14. | " " A | 0.129 | " | 0.129 | " |
| 15. | " " A | 0.129 | " | 0.127[2] | " |
| 16. | 2 gram steel No. 1 + 0.0173 gram. cryst. sodium phosphate | 0.115 | " | 0.116 | " |
| 17. | 2 gram steel No. 3 + 0.0231 gram cryst. sodium phosphate | 0.132 | " | 0.133 | " |
| 18.<br>19. | 1 gram cast iron | 1.75 | " | 1.743<br>1.767 | "<br>" |
| 20.<br>21. | 1 " " " | 1.79 | " | 1.761<br>1.782 | "<br>" |
| 22.<br>23. | 1 " " " dissolved in aqua regia | | " | 1.755<br>1.743 | "<br>" |
| 24.<br>25. | 1 " " " " as for steel | | " | 1.750<br>1.745 | "<br>" |

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[1] Determination by W. A. Noyes.

[2] With fresh, colorless, molybdic solution.

These determinations furnish, we believe, satisfactory proof that the method which has been described, secures a practically complete precipitation of the phosphorus, even when the amount present is only 0.02 per cent., and also that the ratio of phosphorus to molybdenum in the solution is constant and independent of the amount of phosphorus present; also that the ratio is not affected by the presence of silicon or arsenic in the solution. The cast iron used contains 0.84 per cent. of silicon. As regards arsenic, we have applied Marsh's test for arsenic to the yellow precipitate obtained from two grams of steel No. 2, and obtained only a very faint arsenic mirror, much fainter than that obtained under the same conditions, from 0.02 mgm. of arsenious oxide. If we suppose the arsenic to have been present in a compound analogous to the phosphorus compound, the molybdenum associated with it would correspond to only 0.0003 per cent. of phosphorus. The determinations with the cast iron also furnish evidence that the conversion of phosphorus into phosphoric acid is as complete by solution in nitric acid and oxidation with potassium permanganate as by solution in aqua regia and evaporation with nitric acid. The volumetric determinations with the cast iron are more accordant than the gravimetric. In view of the great difficulties known to exist in the way of securing pure magnesium pyrophosphate, we believe the volumetric determination will usually be found to be more accurate.

TERRE HAUTE, December 20, 1894.

# THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.[1]

BY THOMAS H. NORTON.

Received December 24, 1894.

I have felt it desirable on this occasion to direct your attention to a brief review of the services which the chemist has thus far rendered in the battle with fire, to the field of investigation still open, to the methods of testing and experimentation in this branch, and to the application of fact already gained to American conditions. In the choice of this subject, I have, in common

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[1] Abridged from the author's opening address before the Section of Chemistry of the American Association for the Advancement of Science, at the Brooklyn Meeting, August, 1894.