The potential of the charge would vary with the atmospheric conditions and with the manner of wiping the flask. By using a linen cloth in very dry weather, it was found possible to produce a charge on a 100 cc.-flask which would require 0.08 gram additional weight to restore equilibrium.

A high charge like this, however, would be rapidly dissipated and the flask would appear to lose weight. It was found that a charge which apparently caused an increase in weight of about 0.01 gram would be retained quite a long time, and one might readily overlook the error which would be thus introduced. It was further found that a small charge would be retained many days on a flask kept in a desiccator. In damp weather a charge would readily pass off and not give rise to an error, but on a very dry day the practice of wiping glassware just before weighing is liable to cause serious errors.

ANALYTICAL NOTES UPON THE ESTIMATION OF PHOSPHORUS IN STEEL.[1]

BY R. W. MAHON.

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CONTENTS.

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[1] In this paper I have recorded a number of experiments upon the estimation of phosphorus in steel. Their subject is a study in detail of the molybdate-magnesia method. Some of the experiments are upon properties of the molybdate precipitate, which are not connected with this method for estimating phosphorus. The concluding pages describe precipitation of phosphoric acid, out of measured quantities of a standard solution of sodium phosphate.

THESE experiments were made with steel of low carbon content (below 0.10). The preparation of the solutions of the steel for the molybdate precipitation applies to soft steel. The remainder is of general application in steel analysis. These steels do not contain arsenic, and I have not considered the separation of arsenic and phosphorus, except incidentally.

THE SAMPLES.

A volume of liquid steel is throughout of practically uniform composition, and the percentage of phosphorus in all parts of it is the same.

LADLE TESTS FROM A TWENTY THOUSAND POUNDS HEAT OF BESSEMER STEEL, WHICH WAS POURED INTO THREE MOLDS.

Test number.	Percentage of phosphorus.	Remarks.
1	0.096 (average)	Sample taken as the steel was about to be poured into the second mold.
2	0.100 "	About to be poured into the third mold.
3	0.098 "	Third mold nearly full.
1	0.098	Another example.
2	0.102	
3	0.102	
4	0.102	

On the other hand, it is sometimes difficult to obtain drillings from a billet or finished shape, which accurately represent the composition. Incorrect opinions have doubtless been drawn of the relation between physical properties and chemical composition, and also with regard to the accuracy of methods, from neglect to remember the facts of segregation. The four samples of steel employed in this work were planed from the surface of billets, rejecting the first portion. The planings from sample No. 1 were mixed and bottled. The others were prepared as follows: The planings were sieved in a coffee strainer, the dust rejected, and the remainder mixed and bottled. The dust for each was about one-twenty-sixth of the whole. Estimations of phosphorus in drillings, made at about twelve places on the surface of the billet from which sample No. 1 was planed, showed that segregation had taken place to a limited extent.

ESTIMATIONS OF PHOSPHORUS IN THE DUST AND COARSER PARTICLES.

Sample number.	Percentage of phosphorus. Coarser planings, average.	Percentage of phosphorus. The dust, average.
2	0.103	0.109
3	0.101	0.100
4	0.108	0.111

The determinations in different parts of the fluid mass, and in the particles of different size planed from billet surfaces, were made by titration of ammonium phosphomolybdate with potash solution. As the point of the plane passes over a portion of the surface at which phosphorus has segregated, more dust is formed than from the remainder of the surface, which is softer and less brittle, and the dust sifted out will be higher in phosphorus, if there is segregation upon the surface. That the more brittle portions of a surface will yield the larger proportion of dust is evident; it has also been referred to by Von Jüptner[1], who quotes experiments of Leopold Schneider.

In spite of slight segregation on some of the surfaces from which samples were planed, they are regarded as fairly uniform owing to their subsequent treatment. This applies to all of the samples but No. 1. I have been able to use some of the results from No. 1, but not all. Continued tilting of the jar containing the sample, concentrated the dust at the bottom. Removal of the fine portion would not appreciably change the percentage of phosphorus, but concentration to three times the original amount would raise the percentage of phosphorus 0.001 per cent., assuming that the phosphorus in both coarse and fine portions for samples Nos. 1 and 2 are the same, both having been planed from the same face.

PROOF FOR ACCURACY OF PROCESS.

After obtaining a solution of the sample in nitric acid and oxidizing it, it is possible to determine the accuracy of the steps in the molybdate-magnesia method, by carrying the pyro-

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[1] Oest. Zeit. Berg u. Hütten., xiv, 159, per *J. Iron and Steel Inst.*, *1896*, No. 2, 439.

phosphate again through the cycle of operations which were performed in the analysis. I have done this and recorded the results in the following table. Each weight of magnesium pyrophosphate used to calculate a percentage of phosphorus mentioned in the table was corrected by fusing with alkaline carbonates, extracting with water and acid, and evaporating to dryness, taking up with acid, and filtering. The residue was the correction, and the filtrate was used for the reprecipitation of ammonium phosphomolybdate. This method of correcting the weight is not the best way, giving corrections slightly too small. It is also unnecessarily tedious. It was used in these few experiments in order to reconvert pyrophosphate into orthophosphate. The carbonates were examined for phosphorus with negative results.

Results Nos. 1, 2, and 3, of column 3, were obtained by titrating ammonium phosphomolybdate precipitates which had been washed with cold water, with potash solution. The precipitates were thrown down from the solution of the orthophosphate obtained as described above. Its acid solution was rendered alkaline by ammonia and then acid by nitric acid, and molybdate solution added at proper temperature. Although these results were satisfactory, others were obtained in which the large quantity of the salts of the fixed alkalies appeared to interfere with success. I therefore performed the experiments of which the results are recorded in the 4th, 5th, and 6th places of column 3. Here each solution was treated with ferric chloride[1] and after a basic acetate precipitation, a solution was prepared from the precipitate by solution in hydrochloric acid which was then employed for the molybdate precipitation after neutralization as in the previous examples. These later molybdate precipitations were always satisfactory. In these also the estimation was made by titration with potash solution. Results 7 and 8, in column 3, were obtained as follows: The weights of magnesium pyrophosphate from which (corrected) the results 7 and 8 of column 2 were calculated, having been fused with alkaline carbonates and solutions prepared from the fusions as described, basic acetate precipitations and then molybdate precipita-

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[1] The amount of ferric chloride used was such that a sum of less than 0.0002 per cent. of phosphorus for ten grams of sample was introduced.

tions were made as described for 4, 5, and 6. In the solution of the molybdate precipitate in ammonia, the phosphorus was precipitated as magnesium ammonium phosphate and finally weighed as before as pyrophosphate, finding a correction to be applied for impurity present, as in the first pyrophosphate. The treatment of the solution of the molybdate precipitate in ammonia, for separation of the trace of iron present in the colloidal state, and the adjustment of the other details necessary to accurate precipitation of magnesium ammonium phosphate, both here and for the first precipitate are identical in all essentials with those employed in estimations giving accurate results, recorded in the longer tables. These details will be described.

The following table contains eight determinations of phosphorus in a sample of steel by the molybdate-magnesia method, and eight re-determinations, using the weights of pyrophosphate as starting-points.

Number of the determination.	Percentage of phosphorus by the molybdate-magnesia method.	Redeterminations using the weights of magnesium pyrophosphate as starting-points.	Remarks.
1	0.104	0.103	By precipitation as ammonium phosphomolybdate, out of the solution of the fusion of the phosphate.
2	0.104	0.102	
3	1.102	0.101	
4	0.103	0.103	By the same method as the first three preceded by a precipitation with basic ferric acetate.
5	0.104	0.103	
6	0.103	0.101	
7	0.102	0.101	By the same method as last three, followed by solution in ammonia, and precipitation with magnesia mixture.
8	0.104	0.102	

I have determined the phosphorus frequently in this sample and consider it to be 0.103. The molybdate-magnesia method may be considered as proceeding to its end in the three following steps:

I. OBTAINING A SOLUTION FROM THE STEEL OF AMMONIUM PHOSPHATE CONTAINING ALL THE PHOSPHORUS AND ONLY A FAINT TRACE OF IRON.

The True Percentage of Phosphorus in Steel and the Result of Analysis.—Methods for estimating phosphorus in steel, involving precipitation as ammonium phosphomolybdate, proceed upon two assumptions: (1) that no phosphorus escapes during solution and (2) that it is all obtained in a precipitable form. It needs only a simple experiment to convince one's self of the fact that nitric acid of 1.135 sp. gr. proposed for use in steel analysis by Drown,[1] dissolves steel without evolution of hydrogen phosphide. I have made such an experiment, and after passing the gases through silver nitrate have made an examination for phosphoric acid with negative result. The nature of the reaction between silver nitrate and hydrogen phosphide is not unknown to us and indeed Von Jüptner[2] has recently familiarized us with it, through his experiments upon a possible difference of the mode of occurrence of phosphorus in steel, using the precipitated silver as a measure of the hydrogen phosphide given off by the action of dilute sulphuric acid on the steel. I have preferred to examine the absorbing solution (after suitable preparation) by the addition of ammonium molybdate.

On the other hand the second assumption upon which the determination of phosphorus in steel rests, namely that all of the phosphorus in the solution of the steel can be obtained in a precipitable form, is not so easy of proof, and indeed in its nature may be regarded as incapable of absolute proof. It can only be affirmed of a given method for preparing a solution of steel for precipitation that it yields the highest percentage of phosphorus, which is obtained by any other procedure. It does not follow that all of the phosphorus in the sample has been obtained. This latter statement could only be made after having made a compound of given content in phosphorus and obtaining the known result by analysis. To complete the proof the compound must have been made in the same manner: in fact it would be steel, and absolutely homogeneous. These are conditions impossible of fulfilment. The statement that all of the phosphorus in the sample had been obtained, could be made only after getting the same result by difference. This presupposes methods for determining the remaining constituents so delicate as to admit of this, a condition to which the art of analysis has not yet attained.

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[1] *Trans. Am. Inst. Min. Eng.*, 18, 90.

[2] *J. Iron and Steel Inst.*, *1897*, No. 1, 224.

Oxidation.—In preparing a steel for precipitation of its phosphorus, after solution in dilute nitric acid, by oxidation, the various oxidants are of unequal value. The experiments in the following table are not to show the impossibility of oxidizing mild steels by the several means mentioned, but only the relative difficulty when compared with potassium permanganate. It is possible that in most of the cases, perhaps in all, the oxidation would be perfect were the action sufficiently long continued, or a sufficiently large amount of the oxidizer used, or if both these conditions were favorable. In each of the experiments of the table, four grams of steel were boiled in seventy cc. of water and thirty cc. of nitric acid (sp. gr. 1.42). The oxidation in question was then attempted, the solution afterwards made ammoniacal and then just acid by nitric acid, and fifty cc. of molybdate solution added to the solution, which was at 75° C. The precipitates were titrated with potash solution.

THE EFFECT OF VARIOUS OXIDANTS UPON THE DILUTE NITRIC ACID SOLUTION OF A STEEL WHOSE PERCENTAGE OF PHOSPHORUS IS 0.108.

Additional means of oxidation, besides the nitric acid employed for solutions of the sample.	Percentage of phosphorus.	Remarks.
None	0.060	The solution was boiled a short time.
"	0.060	The solution was boiled a short time.
"	0.075	The solution was boiled a long time.
Hydrochloric acid	0.081	The solution boiled, hydrochloric acid added and again boiled.
" "	0.085	
Potassium chlorate	....	A small quantity of the crystals. A very defective precipitation.
Potassium chlorate and hydrochloric acid	0.107	Thirteen grams of crystals. Hydrochloric acid to dissolve precipitated oxides of manganese.
Bromine water	0.073	
" "	0.062	
Sodium peroxide	0.083	A considerable quantity of the solid substance.
Hydrogen dioxide	0.084	A few cc.; strength unknown.
Hydrogen dioxide and hydrochloric acid	0.090	Added alternately in small quantities.
Hydrogen dioxide	0.109	Sixty cc.; a few cc. at each addition.
Chromic acid	0.094	A few cc. of nitric acid, sp. gr. 1.42, saturated with chromic acid.
Potassium bichromate	0.079	A few cc. of water, saturated with potassium bichromate.
Baked on steam-bath for several days at about 80°C.	0.108 0.107	Taken up with hydrochloric acid, and boiled down; then boiled down twice with nitric acid.

Precipitation of Ammonium Phosphomolybdate.—Each of the determinations by the molybdate-magnesia method was made upon ten grams, in two quantities of five grams each. Shimer[1] originally evaporated the solution, after solution of the steel, oxidation by potassium permanganate, and solution of the precipitated oxides in hydrochloric acid, using the filtrate from the silicon determination for phosphorus. The first published reference to the use of hydrochloric acid for dissolving the oxides of manganese, followed without evaporation by neutralization with ammonia, slight acidification with nitric acid and precipitation of ammonium phosphomolybdate, which I have been able to find, is that of H. Wdowiszewski.[2] He was careful to use only a small quantity of hydrochloric acid.

My precipitations were made in two ways: One (A) by dissolving the precipitated oxides of manganese in hydrochloric acid, cooling the solution and adding ammonia until a stiff mush is obtained, then adding nitric acid in excess, and precipitating by adding fifty cc. of molybdate solution to the solution of the steel which is at 75° C. The free acid present expressed as nitric acid of 1.42 sp. gr. in cc., was for this method about thirty cc., half of this being contained in the solution of the steel and half in the molybdate solution added, conditions of precipitation as to precipitant in excess and free acid, far within the limits of safety described by Hundeshagen.[3] I find among the experiments of Fresenius[4] upon this subject, one in which the same result in phosphoric acid, 0.0208 gram, was obtained when precipitating by magnesia mixture directly from a certain volume of sodium phosphate solution, properly prepared as to ammonium chloride content, and with the addition of ammonia; and also after the precipitation as ammonium phosphomolybdate from an equal volume of phosphate solution, redissolving and reprecipitating by magnesia mixture as before. He added fifty cc. of molybdate solution in effecting the precipitation of phosphoric acid, having first added forty cc. of nitric acid of 1.37 sp. gr. Here a perfectly accurate precipitation was made in presence of forty-seven grams of nitric acid (HNO_3). In my (A) precipita-

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[1] *Am. Inst. Min. Eng.*, *1888.*

[2] *Stahl und Eisen*, 12, *1892*, 381 per *J. Soc. Chem. Ind.*, *1892*, 845.

[3] *Ztschr. anal. Chem.*, 28, 141.

[4] *Ibid.*, 3, 446.

tions there were approximately thirty grams of nitric acid (HNO_3) present. In (B) fifteen grams approximately.

Fresenius' well-known molybdate solution recipe—molybdic acid one part, ammonia of 0.96 sp. gr. four parts, and nitric acid of 1.20 sp. gr. fifteen parts—is the one used in my experiments; *viz.*, molybdic acid 100 grams, ammonia of 0.90 sp. gr. 200 cc., water 200 cc., and nitric acid of 1.20 sp. gr. 1250 cc.

Slight agitation in unstoppered Erlenmeyer flasks, and standing ten minutes, causes perfect precipitation. Six precipitates, from five grams of steel each, were filtered in ten minutes. These were heated in covered flasks to 75° C. and then allowed to stand at temperature of room, over night. All remained clear. Six others were filtered in ten minutes, and their filtrates heated to 75° C. for eighteen hours, all remaining clear. One precipitate from five grams was filtered in ten minutes, and one in six hours. These two precipitates, when titrated, gave:

	Per cent. of phosphorus.
Precipitate filtered in ten minutes	0.103
" " " six hours	0.103

The other way (B) of precipitating ammonium phosphomolybdate, I have described,[1] suggesting it as available for a rapid method.[2]

According to this way of working, the steel is dissolved and oxidized as before; redissolving the precipitated oxides resulting from the addition of three cc. of a saturated solution of potassium permanganate used for oxidation, with ten cc. of hydrochloric acid 1.20 sp. gr. The precipitation is made almost immediately upon removal from lamp, by pouring a mixture of fifty cc. of molybdate solution and fifteen cc. ammonia of 0.900 sp. gr. into the solution. The precipitation here is even more rapid than by method A.

Note on the Difference in Ammonium Phosphomolybdate Precipitate by Methods A and B.—When ammonium phosphomolybdate is titrated with potash solution, if the precipitate is obtained by method B, the results are slightly higher than when obtained by

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[1] This Journal, 19, 792.

[2] I have recently seen for the first time some experiments of Albert Attenberg, *Land. Versuchstat.*, 26, 423, as abstracted in *Ztschr. anal. Chem.*, 21, 568. He added molybdate solution to the solution of the phosphate, and then boiled the mixture with constant stirring. Another device which he suggested for rapid precipitation, was using neutral molybdate solution. His paper gives no results by this latter modification.

method A, as reported in the paper above referred to. This depends on some molybdate being carried down with the precipitate. The cause of this is its rapid formation, enclosing molybdate, and not on account of the precipitation of molybdic acid as such. The precipitation of molybdic acid is seen when the molybdate solution and ammonia mixture is rapidly poured into the solution of the steel, the latter being at a temperature of 105° C., without taking pains to direct the stream into the center. Where it runs down the sides of the flask into the solution, molybdic acid is seen to separate in quantity, and again to go into solution when the flask is agitated, leaving a clear solution, out of which ammonium phosphomolybdate precipitates.

That B gives slightly higher results than A when titrating with potash solution, does not necessarily arise from more molybdate present in the precipitates in the first case. The cause might be, it is possible to imagine, a molecule formed with more free acid content, hydrochloric or nitric, than the two molecules mentioned by Hundeshagen.[1] It can, however, be shown that the difference arises from the first cause, by estimations of phosphorus in a standard steel, using three methods, and employing precipitates formed in both ways.

TABLE EXPLAINING THE DIFFERENCE OF RESULTS BY A AND B.

	By caustic potash.	By weight of precipitate, dried at 110° C.	By potassium permanganate.
A	0.108	0.108 0.109	0.109 0.109
B	0.110	0.112 0.110	0.112 0.110

The difference in percentage of phosphorus found by direct treatment of molybdate precipitate is not dependent, however, upon the difference in the method of neutralization employed, but upon the temperature of precipitation, as can be proved by precipitating at 105° C. after neutralization in the older way, and after neutralization in the newer way by precipitating at 75° C.

	Temperature of precipitation.	Percentage of phosphorus found.
Old method of neutralization	105° C.	0.111
New " " "	75° C.	0.108

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[1] *Loc. cit.*

WASHING AMMONIUM PHOSPHOMOLYBDATE.

Number.	Percentage of phosphorus found.[1]	True percentage of phosphorus.	Method of precipitation.	The washing.
1	0.107	0.108	A	850 cc. of cold water.
2	0.105	0.108	A	850 cc. " " "
3	0.107	0.110	B	1000 cc. " " "
4	0.107	0.110	B	1000 cc. " " "
5	0.062	0.108	A	1125 cc. " two per cent. nitric acid.
6	0.039	0.108	A	1125 cc. " two per cent. nitric acid and then with 110 cc. of cold water.
7	0.097	0.110	B	75 cc. of cold water, then 1000 cc. of two per cent. nitric acid, then 200 cc. cold water.
8	0.091	0.110	B	225 cc. of cold water, then 1000 cc. of two per cent. nitric acid, then 300 cc. cold water.
9	0.108	0.108	A	200 cc. of two per cent. nitric acid, then 75 cc. cold water.

These were made with the same sample, and 0.108 and 0.110 denote the results of accurate determinations when titrating precipitates obtained by methods A and B respectively.

Isbert and Stutzer[1] first used cold water to wash the molybdate precipitate. Their results show no loss when washing with 500 cc., and but a slight loss when one liter is used. See Nos. 1 to 4 inclusive, in which the results are slightly lower than those obtained by washing with one-fifth or one-fourth of the mentioned quantities, as in an actual estimation. It was only in preparing precipitates for titration with potash solution that water was the washing fluid.

In dilute nitric acid the molybdate precipitate is much more soluble. (See No. 5.) In this one an empty paper was washed with the same washing fluid, and the result used as a correction.

When a copious washing with nitric acid is followed by a washing with water, the solubility is even more marked; in the latter case being accompanied by a visible running of some of the precipitate through the paper. (See Nos. 6 to 8 inclusive.) These figures are evidently not the result of simple solution, but of decomposition from prolonged washing, a decomposition

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[1] *Ztschr. anal. Chem.*, 26, 584.

rendered more apparent and perhaps increased by subsequently washing with water. Otherwise washing in moderation with dilute nitric acid would dissolve less than in the foregoing examples, but a still appreciable quantity of the precipitate. Actually, washing in moderation with two per cent. nitric acid, does not dissolve any of the precipitate. (See No. 9.) Two hundred cc. of dilute nitric acid is an unnecessarily large quantity to employ.

Re-solution of Molybdate Precipitate.—The absolute separation of small quantities of phosphorus and large quantities of iron by one precipitation of ammonium phosphomolybdate, washing with dilute nitric acid is impossible.

WEIGHTS OF FERRIC OXIDE RETAINED BY THE PRECIPITATE FROM FIVE GRAMS OF STEEL.

Precipitation.		Weights of ferric oxide.
A	1	0.0016
	2	0.0017
B	1	0.0015
	2	0.0015

This iron present in the colloidal condition in the ammoniacal solution of the molybdate precipitate separating upon evaporation, and carries down with it about two-tenths of a milligram of phosphorus in these steels. It is my custom to filter at this point,[1] redissolve the iron in hydrochloric acid, make its solution ammoniacal, and then faintly acid with nitric acid; now add a few cc. of molybdate solution. The small precipitate having been filtered and redissolved in ammonia, its solution running into the main quantity of ammonium phosphate, this is to be evaporated, until the smell of ammonia has disappeared and the bulk is sufficiently reduced.

The solution is now prepared for precipitation by adding the quantity of hydrochloric acid required for the particular case, and then ammonia from a burette, finally obtaining a faintly ammoniacal solution which is diluted to the volume wished, and magnesia mixture dropped in, with constant stirring, followed by the addition of ammonia in the same manner.[2]

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[1] It is impossible to give an intelligible description of experiments upon this theme without mentioning familiar details.

[2] Blair's Chemical Analysis of Iron, First Edition, p. 82, prescribes the addition of strong ammonia, in the proportion of one-fourth of the final volume. Such a solution

II. THE ACCURATE PRECIPITATION OF PHOSPHORUS AS MAGNESIUM AMMONIUM PHOSPHATE.

The use of magnesium chloride, ammonium chloride, and ammonia. The same washing fluid was used throughout: ammonia of 7.25 per cent. (that is, water three volumes, ammonia, sp. gr. 0.90, one volume) unless otherwise mentioned.

Two magnesia mixtures were used. The first was made from magnesia, hydrochloric acid, and ammonia, and the magnesium chloride and ammonium chloride per cc. determined. This mixture is called 1, in the tables. The second magnesia mixture called 2 in the tables, is described on page 51 of "Blair's Chemical Analysis of Iron," first edition. Fifty-eight grams of ammonium chloride in two liters were used instead of the quantity called for by that recipe.

Magnesia Mixture, Containing Enough Ammonia to Impart a Decided Odor.

	No. 1.	No. 2.
Magnesium Chloride, crystallized	66 grams.	110 grams.
Ammonium Chloride	69 "	58 "
Volume	2 liters.	2 liters.

contains 7.25 per cent. of free ammonia (NH_3). This is the amount of ammonia added in each of the following experiments, unless otherwise mentioned. Two and five-tenths per cent. of free ammonia (NH_3) in solution and for wash is probably most used for this precipitate—Fresenius' Quantitative Analysis; Fresenius: *Ztschr. anal. Chem.*, **6**, 403; Wagner and his coworkers: *Ibid* **19**, 444 and **21**, 353; etc. It is the strength used in the official method for agricultural analysis in Germany, and is described in Bulletin 46, U. S. Department of Agriculture as part of the official method for agricultural analysis in this country.

THE USE OF MAGNESIUM CHLORIDE, AMMONIUM CHLORIDE, AND AMMONIA.

Number of the estimation.	Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Magnesia mixture used.	Remarks.
1	1	0.104	0.043	0.57	0.010	60	125	1	Magnesium chloride in small excess. Small quantity of ammonium chloride present.
2	1	0.103	0.043	0.57	0.007	76	120	1	
3	1	0.102	0.043	1.07	0.014	76	120	1	
4	1	0.104	0.043	1.42	0.019	76	90	1	
5	3	0.100	0.086	1.14	0.021	54	128	1	
6	3	0.101	0.086	1.14	0.018	62	128	1	
7	3	0.101	0.086	1.14	0.017	69	126	1	
8	3	0.099	0.058	0.99	0.016	60	105	1	
9	3	0.100	0.086	1.14	0.019	60	130	1	
10	3	0.103	0.086	1.14	0.019	60	125	1	
11	3	0.100	0.058	0.99	0.016	60	130	1	
12	4	0.108	0.077	0.70	0.023	30	110	2	
13	4	0.108	0.077	0.70	0.008	87	100	2	
14	4	0.114	0.090	0.10	0.002	60	120	2	
15	4	0.117	0.090	0.10	0.002	60	120	2	
16	1	0.103	0.043	9.57	0.124	77	98	1	Magnesium chloride in small excess. Moderate quantity of ammonium chloride present.
17	1	0.101	0.043	5.92	0.099	60	130	1	
18	1	0.103	0.043	5.92	0.099	60	130	1	
19	1	0.102	0.043	5.92	0.099	60	130	1	
20	1	0.104	0.043	5.92	0.099	60	130	1	
21	1	0.104	0.043	5.91	0.089	67	130	1	
22	2	0.102	0.043	6.25	0.142	60	112	1	
23	2	0.101	0.043	6.25	0.142	60	112	1	
24	2	0.102	0.043	6.25	0.142	60	112	1	
25	3	0.100	0.086	5.15	0.067	77	147	1	
26	3	0.100	0.086	5.15	0.067	77	144	1	
27	3	0.100	0.058	11.00	0.138	80	120	1	
28	3	0.099	0.058	11.00	0.130	80	130	1	
29	4	0.106	0.077	10.79	0.135	80	100	2	
30	4	0.109	0.077	10.79	0.124	87	138	2	
31	4	0.109	0.077	25.79	0.143	180	110	2	Magnesium chloride in small excess. Large quantity of ammonium chloride present.
32	4	0.109	0.077	25.79	0.143	180	110	2	
33	4	0.116	0.255	1.00	0.025	41	110	2	Magnesium chloride in large excess. Small quantity of ammonium chloride present.
34	4	0.111	0.180	1.65	0.025	57	110	1	
35	4	0.111	0.180	1.65	0.025	60	110	1	

36	4	0.114	0.255	10.00	0.105	95	110	2	Magnesium chloride in large excess. Moderate quantity of ammonium chloride present.
37	4	0.110	0.255	10.00	0.097	103	110	2	
38	3	0.100	0.180	10.18	0.087	117	137	1	
39	3	0.103	0.180	10.18	0.085	120	115	1	
40	3	0.103	0.180	11.00	0.103	107	108	1	
41	3	0.099	0.180	11.00	0.103	107	118	1	
42	4	0.110	0.255	25.00	0.170	153	140	2	Magnesium chloride in large excess. Large quantity of ammonium chloride present.
43	4	0.110	0.255	25.00	0.170	153	140	2	
44	2	0.104	0.130	6.00	0.081	74	90	1	Use of ammonia of 2.5 per cent. in solution of customary size.
45	2	0.102	0.130	6.00	0.090	67	90	1	
46	2	0.104	0.130	6.00	0.090	67	90	1	
47	4	0.101	0.077	20.00	0.070	288	115	2	Large volume for precipitation. Percentage of ammonia 2.5
48	4	0.111	0.077	0.80	0.003	288	110	2	
49	4	0.105	0.281	20.00	0.070	288	115	2	
50	4	0.112	0.077	0.80	0.003	288	110	2	Large volume for precipitation.
51	4	0.119	0.077	0.80	0.003	288	110	2	
52	4	0.111	0.077	10.00	0.035	288	100	2	
53	4	0.105	0.077	10.00	0.035	288	100	2	
54	1	0.098	0.043	25.00	0.104	240	100	1	
55	1	0.100	0.043	25.00	0.104	240	100	1	
56	4	0.101	0.077	20.00	0.070	288	77	2	
57	4	0.103	0.077	20.00	0.070	288	117	2	
58	4	0.110	0.255	10.00	0.035	288	100	2	
59	4	0.111	0.255	10.00	0.035	288	100	2	
60	4	0.105	0.255	20.00	0.070	288	92	2	
61	4	0.106	0.255	20.00	0.070	288	72	2	
62	4	0.109	0.077	5.00	0.083	60	110	2	Magnesium chloride added somewhat slower than heretofore.
63	4	0.107	0.077	5.00	0.083	60	125	2	
64	4	0.111	0.077	5.00	0.083	60	110	2	
65	4	0.107	0.306	6.00	0.084	71	155	2	
66	4	0.107	0.306	6.00	0.084	71	125	2	
67	4	0.107	0.077	5.60	0.093	60	140	2	Magnesium chloride added as in last five. Time of precipitation, 67 and 68—2 hours, 69 and 70—1 hour.
68	4	0.107	0.077	5.60	0.093	60	140	2	
69	4	0.110	0.306	5.90	0.077	77	130	2	
70	4	0.110	0.306	5.90	0.077	77	130	2	
71	.	0.0014	0.043	6.00	.....	60	150	.	Precipitated in 30 minutes.
72	.	0.0032	0.043	6.00	.....	60	165	.	
73	.	0.0026	0.043	6.00	.....	60	170	.	
74	.	0.0024	0.043	6.00	.....	60	110	.	Precipitated in 1 hour.
75	.	0.0014	0.043	6.00	.....	60	110	.	
76	.	0.0026	0.043	6.00	.....	60	110	.	

When magnesium chloride is used in small excess, the result is practically the same, whether ammonium chloride be present in small, moderate, or large quantity. Thus for samples Nos. 1, 3, and 4, the means are :

1.	3.	4.	Sample number.
0.1033	0.1006	0.1080[1]	Small quantity of ammonium chloride present.
0.1028	0.0998	0.1075	Moderate " " " " "
......	......	0.1090	Large " " " " "

Error can however occur when using magnesium chloride in small excess if the amount of ammonium chloride be sufficiently reduced. Estimations Nos. 14 and 15, on sample No. 4, show 0.114 and 0.117.

When magnesium chloride is added in large excess error is more frequently introduced. Thus for samples Nos. 3 and 4, the means are :

3.	4.	Sample number.
......	0.1127	Small quantity of ammonium chloride present.
0.1013	0.1120	Moderate " " " " "
......	0.1100	Large " " " " "

The figures above for sample No. 4 also show the lessening of plus error brought about by the presence of ammonium chloride in proper quantity.

The larger the excess of magnesium chloride the more rapid the precipitation, and the more ammonium chloride present the slower the precipitation. As too great rapidity causes inaccuracy, and as ammonium chloride solution has a solvent action upon magnesium ammmonium phosphate, it follows that these ingredients must be adjusted within certain limits. In other words, the proper amount of ammonium chloride is dependent upon the excess of magnesium chloride used. That the same amount of ammonium chloride does not prevent plus error irrespective of the excess of magnesium chloride is illustrated by estimation Nos. 36 to 41. Nos. 36 and 37 give a mean of 0.112 instead of the true percentage 0.108. Nos. 38 to 41 inclusive give a mean of 0.101 instead of 0.100. Here the amounts of ammonium chloride are nearly equal, and the magnesium chloride in excess, much greater for Nos. 36 and 37. All the results thus far discussed will be seen by a reference to

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[1] Nos. 14 and 15 are not included.

the table to have been obtained when precipitating in solutions of customary size. Estimations Nos. 50 to 61 inclusive were made, effecting the precipitation in large solution. These estimations include examples with small and large excess of magnesia mixture, in presence of ammonium chloride in varied amount. Although useless as suggestions for analysis, they are interesting as showing the variations caused by variations in magnesium chloride and ammonium chloride. Detailed comment is unnecessary; the dissolving effect of ammonium chloride is a chief feature, increasing with the concentration, and lessening with the excess of magnesium chloride. By an exact balance, accurate results would be obtained. But this is uncertain of attainment, and in the twelve examples considered, has not been reached in one. Either the ammonium salt solution was too concentrated for the excess of magnesia and some weight of precipitate was dissolved or the concentration of ammonium salt solution was too slight and the precipitate was contaminated by the excess of the precipitant.

Indeed in Nos. 52 and 53, supposed to be executed identically, accidental variation has caused one to fall above and the other below the truth.

	Percentage of phosphorus.
No. 52	0.111
" 53	0.105
True percentage	0.108

Comparisons of Nos. 50 and 51 with No. 13, and then with Nos. 14 and 15 show that it is not the weight alone, but also the concentration of the solution of ammonium chloride which prevents coprecipitation of magnesia.

Number of the estimation.	Percentage of phosphorus.	Ammonium chloride present. Gram.	Ammonium chloride per cc. Gram.
50	0.112	0.80	0.003
51	0.119	0.80	0.003
13	0.108	0.70	0.008
14	0.114	0.10	0.002
15	0.117	0.10	0.002

In the estimations thus far and in those to be described, the filtrate and wash-water was examined for phosphoric acid, usually only with the finding of traces (less than 0.001 per cent. phosphorus), unless experiments had been made in similar cases, showing this to be unnecessary. The method was: boiling down until ammonia was driven off, acidifying and adding a few cc. of molybdate solution. One-tenth of a milligram of phosphorus can be detected thus, as can be seen by examining a blank, to which this quantity of phosphorus had been added, as sodium phosphate.

The filtrates from some of the twelve just described, were examined for phosphorus, with the following results:

	50	51	57	58	59	60	61
Percentage of phosphorus in the filtrate	0.000	0.000	0.007	0.000	0.000	0.004	0.001

Nos. 44 to 49 inclusive describe estimations, where the percentage of ammonia is two and five-tenths in the solutions for precipitation. Nos. 44, 45, and 46 give a mean of 0.1033; Nos. 22, 23, and 24 give 0.1017. The first slightly higher, on account of greater excess of precipitant, and a lesser concentration of ammonium chloride, and showing no result from lesser strength of ammonia. The latter mean is correct, and the first has a plus error of 0.0016. Approximately the same relations (except that the same strength of ammonia is present in the estimations now to be compared) exist between Nos. 38 to 41 inclusive, and Nos. 27 and 28.

Nos. 47 to 49 inclusive, like Nos. 50 to 61 inclusive, were obtained by precipitating in large volume. The same idea of variations in the amount of precipitant and of ammonium chloride, is carried out here. The results, like the corresponding ones in the other series, show no variations due to difference of strength of ammonia present.

No. 47,	0.101	No. 48,	0.111	No. 49,	0.105
" 56,	0.101	" 50,	0.112	" 60,	0.105

Nos. 62 to 66 inclusive give results obtained by adding magnesia mixture even slower than in previous cases, as follows: something more than the theoretical amount, dropped slowly in as usual and the remainder added in the same manner after an interval.

No average difference between properly made previous determinations, and Nos. 62 to 66 inclusive, is apparent.

The time of precipitation is part of the general subject of use of magnesium chloride and ammonium chloride, for it depends upon the quantities of those salts present.

Nos. 67 to 70 inclusive illustrate the effect of excess of magnesium chloride in hastening precipitation. While Nos. 67 and 68 are slightly below the true percentage, in Nos. 69 and 70 while perfect precipitation was obtained in one hour, the precipitant was dropped in, apparently, somewhat too rapidly. But the effect of magnesium chloride in hastening and of ammonium chloride in retarding precipitation is a visible result, which I have often observed in carrying out a number of estimations simultaneously, with these details differing. In Nos. 71 to 76 inclusive, I have only recorded the phosphorus found in the filtrates.

III. OBTAINING THE CORRECT WEIGHT OF MAGNESIUM PYROPHOSPHATE.

Eleven cm. filter-paper seems to be preferable to a smaller size, for the magnesium ammonium phosphate filtration, particles of the precipitate being less liable to crawl above its edge. The dangerous operation of drying, and burning the paper separately, should be abandoned, in favor of enfolding the precipitate in its still slightly moist paper, and burning in an inclined crucible without lid. I always use the end of a stout platinum wire to break up the precipitate, after the carbon of the paper is almost consumed. This operation can be so carried out as to give rise to no error. There are always three impurities in the magnesium pyrophosphate. These are silica, ferric oxide, and molybdic acid; the last if the precipitation has been made in presence of molybdic acid. Silica and ferric oxide are best separated by hot, very dilute hydrochloric acid. Every precipitate derived from steel was corrected for these impurities. Their sum is usually a fraction of one milligram. The weight of molybdic acid, after ignition before the blast-lamp, can be neglected.[1]

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[1] Drown, in a paper by George E. Thackray, "A Comparison of Recent Phosphorus Determinations in Steel," *Trans. Amer. Inst. Min. Eng.*, October, 1895, describes his method of making two phosphorus determinations, published in the paper. The following is a part of the description: "Dissolve the ammonium magnesium phosphate in hydrochloric acid and into this solution pass sulphuretted hydrogen for three or four hours, the liquid being nearly boiling the greater part of the time. After filtering off the molybdenum sulphide, and any arsenic which may be present, the ammonium magnesium phosphate is again precipitated by ammonia, with the addition of a little more magnesia mixture." Three determinations of phosphorus in sample No. 4, carried out as I describe them, the first precipitate of magnesium ammonium phosphate being redissolved and treated according to the above quotation resulted as follows: 0.109, 0.108, and 0.109.

It is one or two-tenths of a milligram. I have determined molybdic acid in these precipitates, in the filtrate from silica and iron, by precipitating by hydrogen sulphide. Two of these were filtered and weighed on asbestos felt in a Gooch crucible, after drying, proving to be a small, doubtful fraction of one milligram. Other precipitates of this impurity by hydrogen sulphide were simply observed. A solution was prepared from forty milligrams of molybdic acid in a little ammonia, and this diluted to one liter. Portions of this were measured off, acidified with hydrochloric acid and having been diluted, treated with hydrogen sulphide gas. The quantity of molybdic acid in ten cc. of this solution if present in a pyrophosphate after ignition before the blast-lamp, would cause an error of 0.001 per cent. phosphorus for ten grams of steel. Ten cc. of the solution however if precipitated as above, give a precipitate, much greater than any derived from these pyrophosphates.

Another way of studying this subject is shown in the estimations carried out with standard sodium phosphate solution, described further on, where the error arising from presence of molybdic acid in the ignited precipitate is proved to be zero.

I have determined phosphorus twice in sample No. 4 filtering magnesium ammonium phosphate on asbestos felt in a Gooch crucible. These determinations are uncorrected for admixed silica and ferric oxide, and each gave 0.109 per cent. phosphorus.

WASHING MAGNESIUM AMMONIUM PHOSPHATE.

Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Magnesia mixture used.	Washing fluid.
1	0.103	0.0432	6.00	0.100	60	250	1	7.25 per cent. ammonia.
1	0.103	0.0432	6.00	0.100	60	250	1	
3	0.096	0.0864	1.20	0.017	69	215	1	2.50 per cent. ammonia.
3	0.099	0.0864	1.20	0.017	69	215	1	
4[1]	0.103	0.077	5.00	0.050	100	220	2	9.67 per cent. ammonia having dissolved in 100 cc. 2.50 grams of ammonium nitrate.
4[1]	0.105	0.051	5.00	0.057	87	240	2	

[1] Blair's Chemical Analysis of Iron, First Edition, p. 82.

The varying figures for ammonium chloride and for magnesium chloride are without significance. Although the last two washing fluids show dissolving power on this precipitate, when used in excessive amount, they are satisfactory as customarily employed, as follows:

Number of the estimation.	Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Percentage of ammonium in solution of precipitation.	Magnesia mixture used.	Washing fluid.
	1	0.104	0.130	6.0	0.10	60	100	7.25	1	2.5 per cent. ammonia.
	1	0.101	0.130	6.0	0.10	60	100	7.25	1	
44	2	0.104	0.130	6.0	0.08	74	90	2.50	1	
45	2	0.102	0.130	6.0	0.09	67	90	2.50	1	
46	2	0.104	0.130	6.0	0.09	67	90	2.50	1	
	1	0.103	0.086	6.0	0.10	60	100	7.25	1	9.67 per cent. ammonia having dissolved in 100 cc. 2.5 grams of ammonium nitrate.
	1	0.103	0.086	6.0	0.10	60	100	7.25	1	
	2	0.103	0.086	6.0	0.11	53	100	7.25	1	
	2	0.101	0.086	6.0	0.10	60	100	7.25	1	
	2	0.103	0.086	6.0	0.09	67	100	7.25	1	

EXPERIMENTS IN ESTIMATING PHOSPHORUS IN SOLUTION OF SODIUM PHOSPHATE.

The solution was prepared from a salt purchased as chemically pure. This was recrystallized, filtered on the suction-pump, and washed once with cold water. The purified salt was dissolved in water and preserved in a ground glass-stoppered bottle, portions of it being filtered as used. Two quantities of twenty cc. each were evaporated to dryness and ignited in a weighed platinum capsule. The weights of phosphorus calculated from the two weights of sodium pyrophosphate obtained were 0.01008 and 0.01008. If these are expressed as percentages of phosphorus obtained by analysis of ten grams of steel, they would be 0.1008 and 0.1006. The following are the determinations of phosphorus in the solution, by precipitation as magnesium ammonium phosphate, using twenty cc. of the filtered solution for each precipitation.

No. 2 magnesium mixture was used in the determinations of the following table, and 7.25 per cent. ammonia for precipitation and washing fluid.

Number of the estimation.	cc. of hydrochloric acid of 1.20 sp. gr.	cc. of magnesia mixture.	Molybdic acid. Gram.	Method of adding magnesia mixture.	Ammonia or magnesia mixture added last.	Volume for precipitation.	Volume of washing fluid.	Weight of magnesium pyrophosphate.	Phosphorus expressed as a percentage for ten grams of steel.
1	8	3	0.61	A	X	60	81	0.0365	0.102
2	7	3	0.61	A	X	60	73	0.0369	0.103
3	7	10	0.61	A	X	67	85	0.0372	0.104
4	7	10	0.61	A	X	67	85	0.0369	0.103
5	7	3	0.00	A	X	60	83	0.0369	0.103
6	7	3	0.00	A	X	60	87	0.0370	0.103
7	7	10	0.00	A	X	67	85	0.0374	0.104
8	7	10	0.61	B	X	60	85	0.0363	0.1011
9	7	10	0.00	B	X	60	90	0.0363	0.1011
10	7	10	0.00	A	X	60	105	0.0381	0.106
11	2	10	0.61	A	X	60	95	0.0373	0.104
12	2	10	0.00	A	X	60	110	0.0382	0.106
13	1	10	0.61	A	X	60	120	0.0387	0.108
14	1	10	0.00	A	X	60	125	0.0434	0.121
15	7	3	0.61	B	Y	73	77	0.0359	0.0999
16	7	10	0.61	B	Y	73	117	0.0357	0.0994
17	7	10	0.61	B	Y	76	85	0.0361	0.1005
18	7	3	0.61	B	Y	76	105	0.0360	0.1002
19	7	10	0.00	B	Y	76	95	0.0357	0.0994
20	7	3	0.00	B	Y	76	95	0.0356	0.0991
21	1	10	0.61	B	Y	76	95	0.0379	0.106
22	1	10	0.00	B	Y	76	95	0.0384	0.107

The approximate weights of molybdic acid given in column 4 of the table were each dissolved in a little ammonia, and added, after filtration, to the phosphate solution. The hydrochloric acid of column 2 was then added, and then gradually ammonia until the solution became ammoniacal. When cold the solutions X were precipitated by the slow addition of magnesia mixture, this being followed by the addition of ammonia of 0.90 sp. gr., one third of the volume of the solution before its addition being dropped in with constant agitation. To the solutions Y the same quantity of ammonia as for X was first added and then the magnesia mixture dropped in.

A and B of the fifth column, denote: A, that the magnesia mixture was slowly dropped into the phosphate solution with constant agitation; B, that the addition of magnesia mixture was made as for A but with intervals of waiting at each half cc.

for the first three cc. added. After the first three cc. the remainder was dropped in continuously. The A additions occupied about one minute each, the B each about one-half hour or more.

In estimating phosphorus in steel by the molybdate-magnesia method, owing to the number of details involved, when separating molybdenum before the final precipitation as magnesium ammonium phosphate, it is difficult to decide whether its removal, in cases uncomplicated by the presence of arsenic, is advantageous or not. Estimations Nos. 1 to 7 inclusive give some light upon this point. Here there is no difference in results whatever, when precipitating with molybdic acid absent, and in presence of 0.61 gram of molybdic acid (approximately the weight present in analyzing steel of about 0.100 per cent. phosphorus, when employing ten grams in an analysis). There is no apparent difference in the results for Nos. 1, 2, 5, and 6, where three cc. of magnesia mixture were used in precipitating, and Nos. 3, 4, and 7, where ten cc. of magnesia mixture were used. This is because the precipitation had largely occurred before the larger excess of magnesium chloride entered the solution. These first seven are slightly too high. Because, although the magnesia mixture was added rather slowly, it was not added slowly enough to entirely eliminate plus error.

As in the first seven, so also in the remaining ones, the several determinations are duplicated, having no molybdic acid present in the solution when making one precipitation and 0.61 gram when making the other precipitation. The true result, as given by the sodium pyrophosphate determinations, being 0.1007, that is, approximately 0.101. Nos. 8 and 9 give this percentage, being results of almost ideal accuracy. The details differ from the first seven only in the rate at which magnesia mixture was dropped in. On the contrary, the rate of dropping in No. 10 was much increased, even over the first seven, and a greater plus error results, than in these.

In examples Nos. 11 to 14 inclusive the effect of decreasing the amount of ammonium chloride is illustrated. By contrasting Nos. 8 and 9 with Nos. 15 to 20 inclusive, the effect of reversing the order of addition of magnesia mixture and ammonia is seen.

	Percentage of phosphorus.
No. 8	0.1011
" 9	0.1011
Mean	0.1011
Sodium pyrophosphate determination 1	0.1008
" " " 2	0.1006
Mean	0.1007
No. 15	0.0999
" 16	0.0994
" 17	0.1005
" 18	0.1002
" 19	0.0994
" 20	0.0991
Mean	0.0998

Nos. 21 and 22 show that even with the order of addition reversed, and with the extremely slow addition of magnesia mixture, the results are too high for large excess of precipitant, when the ammonium chloride is sufficiently reduced.

When magnesium chloride is added not in excess to solutions containing only a small quantity of free ammonia, or is thus added to those containing a large amount of free ammonia, some distinct quantity of phosphoric acid remains unprecipitated, as is well known. The same thing is true if an excess of magnesium chloride is added to a solution containing a large amount of free ammonia. Compare Nos. 8 and 9 with Nos. 15 to 20 inclusive. Filtrates from precipitations like Nos. 8 and 9 have, when examined for phosphoric acid, shown no trace, whereas in the class of precipitations represented by Nos. 15 to 20 inclusive a distinct reaction for phosphoric acid is obtained. This is not to be regarded as the solution of magnesium ammonium phosphate as such, but as the result of partial decomposition of this precipitate, at the moment of its formation by ammonia, with formation of ammonium phosphate and magnesia. The magnesia is dissolved by ammonium chloride if this is present in sufficient quantity, otherwise it remains to introduce plus error.

In large quantity of free ammonia then, the tendency to this reaction is more marked than in solutions containing only a small quantity of free ammonia. Hence the reaction occurs only in nearly neutral solution when not reinforced by excess of magnesium chloride, whereas in solutions strongly ammoniacal, it occurs even if magnesium chloride is present in large excess. When magnesium chloride is added in excess too rapidly, or when the amount of ammonium chloride is much reduced, for either order of addition of ammonia and magnesium chloride some magnesia is precipitated. This occurs for too rapid addition, because as we may consider under this condition, a phosphate of magnesium is formed containing more magnesia than magnesium ammonium phosphate. It is conceivable that this may remain unchanged, giving too great weight after ignition, but I prefer to regard the reaction here, as being like that in the cases already considered. Thus the abnormal precipitate at the moment of its formation is partially decomposed by ammonia, and magnesium ammonium phosphate and magnesia are formed. If there is enough ammonium chloride present, and if the magnesium chloride is not added too fast, giving too rapid formation, the magnesia precipitated is redissolved as in cases already described. I do not regard the contamination by excess of magnesia mixture as mechanical.[1] The relative bulks of precipitates in Nos. 8 to 14 inclusive, a series carried out simultaneously, are against this idea, No. 14 being at least ten times the bulk of Nos. 8 or 9. Nos. 11 to 14 inclusive were the larger, and No. 14 the largest of the series. It is true that a bulky precipitate carries down more salt from solution than a crystalline one. In this regard the contamination is in part perhaps mechanical, but the bulk itself is not the chief cause, but an effect of contamination. Not only the size of such precipitates but their character show this.

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[1] Gooch : *Am. Chem. J.*, 1, 391.