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THE ESTIMATION OF ALUMINA AND FERRIC OXIDE IN NATURAL PHOSPHATES.¹

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THE search for an accurate and rapid method for the determination of alumina and iron oxide in the presence of phosphoric acid has occupied the attention of analysts for years, and many methods have been proposed for this difficult operation. It may be said generally that even those methods that have stood the tests of extended use have not escaped severe criticism; they are only accurate within narrow and rigidly defined limits or they are tedious and time-consuming.

Aside from its interest from the scientific point of view, this subject is of importance in its technical and commercial aspects. The value of raw mineral phosphates, which, in the United States alone, for the year 1893, Wiley estimates at \$4,157,070,² is determined largely by their content of alumina and iron.

In phosphatic slags the estimation of these oxides is more difficult, though possibly not so important.

SOURCES OF ERROR IN THE OLDER METHODS.

The Glaser alcohol, the acetate with its various modifications, and the caustic alkali, methods as carried out by Lasne, Lichtschlag, and by Gladding, have all been severely criticized and the following sources of error pointed out by various observers:³

1. In the Glaser alcohol method, the precipitation of manganese with the iron and aluminum phosphates, and solubility of the phosphates in the wash-water. Probably the manganese can be eliminated by a second precipitation in the presence of a large amount of ammonium chloride. Possibly the presence of a large amount of ammonium sulphate may also effect the accuracy of this method, in those cases where the excess of ammonia is com-

¹ Abstract of Thesis presented to the Faculty of the Graduate School of Columbian University and accepted for the degree of Master of Science, June, 1898. Presented to the American Chemical Society, Boston Meeting, 1898.

² U. S. Department of Agriculture, Yearbook, 1894.

³ Wiley's "Principles and Practice of Agricultural Analysis," Vol. II, pp. 24, *et seq.*

pletely removed by boiling. Aluminum phosphate is noticeably soluble in a strong sulphate solution, which is neutral or faintly acid from SO_3 .

2. In the acetate method and its variations, the precipitation of the lime with the iron and aluminum phosphates, solubility of aluminum phosphate in cold acetate solutions, solubility and dissociation of iron and aluminum phosphates in water,¹ also when the phosphates are fused with sodium carbonate, and the iron determined by precipitation with ammonia, the contamination of the iron with calcium phosphate, which is not always entirely decomposed by fusion. Of these the most serious sources of error are the first and the last mentioned.

3. In the caustic alkali methods, there is danger of some of the aluminum being held by the voluminous precipitate produced by the alkali; there is also danger of alumina being precipitated if much carbon dioxide is absorbed; Lasne and Lichtschlag have shown that while the method is long it gives accurate results if properly conducted. Blaltner and Brasseur² have recently investigated the more important methods and conclude:

“The acetate method should be discontinued; figures for alumina are nearly always too low.”

Glaser method (alcohol) gives accurate results in the absence of manganese.

The caustic soda method, as carried out by Lasne, gives exact results. Gruber's and Gladding's methods are condemned.

In view of these many sources of error in the conventional methods, considerable time has been devoted to the study of a method that, it is hoped, is free from most of the above-mentioned objections. It is an adaptation, so far as possible, of the good points of the present best methods. From the precipitating reagent, it may be designated

THE THIOSULPHATE METHOD.

The use of a soluble thiosulphate for the separation of alumina from iron and aluminum from several other metals seems to be due to G. Chancel.³ Later it was used by Stead and by Car-

¹ *Chem. Ztg.* (1897), p. 264; also Fresenius.

² *Bull. Soc. Chim.* [3], 17, 18, No. 15.

³ *Compt. rend.*, 46, 98.

not;¹ by the latter for the separation of aluminum as phosphate, in the presence of ammonium acetate, from iron. Lasne² also uses it to precipitate aluminum phosphate in the presence of ammonium acetate, after removing iron, lime, etc., with caustic soda.

From the available literature on the subject it seems that a method based on the separation of aluminum phosphate from iron and lime by a thiosulphate and ammonium chloride alone, may be used for the determination of aluminum in the common natural phosphates.

Considerable work has been done with the method to gain familiarity with it and to test its applicability under various conditions and in the presence of various salts. For this work a chemically pure aluminum sulphate was prepared in which alumina has been carefully determined. This salt was used for all the tests.

The preliminary work under varying conditions, following the method as laid down by Chancel and by Carnot, did not always give concordant results, frequently being low. A brief study suggested the cause of this, and the addition of a considerable quantity of ammonium chloride led to much better results. The principle upon which the method is based is the insolubility of aluminum phosphate in a strong neutral solution of ammonium chloride. The thiosulphate has nothing to do with the precipitation, except that it is an exact method of obtaining the desired neutrality. Thomson³ has devised a method in which he makes use of this principle, neutralizing with ammonia, using a delicate indicator to determine neutrality.

Study of the Proposed Method.—One of the first problems presented in the study of any method for the determination of alumina as phosphate is the composition of the ignited phosphate. Observers do not agree as to this. While all agree that the normal phosphate is only obtained in the presence of an excess of phosphoric acid, they do not agree that it is always obtained, even under these conditions.⁴

¹ Blair's "Chemical Analysis of Iron," second edition, 185, 186.

² *Bull. Soc. Chim.*, 15, 118.

³ *J. Soc. Chem. Ind.*, 15, 868.

⁴ *Chem. Ztg.* (1897), pp. 264, and 21, 116; Wiley's "Principles and Practice of Agricultural Analysis," Vol. II, p. 24; Blair's "Chemical Analysis of Iron," second edition, 185; S. C. Agr. Expt. Sta., Bull. No. 2.

Wash Solutions.—It seems that the solution of this problem can only be obtained by a study of the solutions used in washing the precipitate. Besides waters of all temperatures, solutions of various salts, such as 5 per cent. ammonium nitrate, ammonium chloride, 1 per cent. ammonium nitrate plus 0.02 per cent. ammonium phosphate, and dilute ammonium acetate, have been proposed and used by many investigators. These various washes possibly account for the variations from the normal, so frequently noted. In the brief mention of some of the observed sources of error in the conventional methods it was shown, by numerous authorities, that the recently precipitated phosphates of iron and aluminum, when freed from adhering salts, are slightly soluble, or rather are dissociated, in water of any temperature. Those who have apparently used water successfully as a wash probably did not wash enough, only three or four times, to remove the adhering salts. Cold ammonium or sodium acetate also slowly dissolves aluminum phosphate.

The effects of the following wash liquors have been studied :

Water at from 60° to 70° C.

5 per cent. ammonium nitrate at from 60° to 70° C.

1 " " " " " " " 60° " 70° C.

5 " " " " and 0.02 per cent. ammonium phosphate at from 60° to 70° C.

Method of Study.—Various quantities of the C. P. aluminum sulphate were placed in a 12-ounce beaker with a solution of 2 grams of ammonium phosphate, the resulting precipitate dissolved in hydrochloric acid, and 25 cc. of a 50 per cent. solution of ammonium chloride added. The solution was then made alkaline with ammonia and the precipitate just dissolved with hydrochloric acid, noting approximately the number of cubic centimeters required after the solution had become acid; the solution was then diluted to about 250 cc., and for each cubic centimeter of hydrochloric acid added to the acid solution 5 cc. of a 50 per cent. solution of ammonium thiosulphate were added dropwise, the beaker covered with a watch-glass, the solution boiled half an hour, filtered, washed, dried, and ignited to constant weight.

The results are given in Table I. All results in the work have been corrected by blank determinations on the reagents

TABLE I.

Wash solution.	Washings.		Al ₂ O ₃ . Theory. Mgs.	Al ₂ O ₃ . Found. Mgs.	Error. Mgs.
	Times.	Volume. cc.			
Water 60° to 70° C.....	40	500	159.7	155.9	-3.8
“ 60° “ 70° C.....	20	250	39.9	38.2	-1.7
5 per cent. ammonium nitrate, 60° to 70° C.....	20	250	39.9	39.8	-0.1
5 “ “ “ 60° to 70° C.....	20	250	79.8	79.6	-0.2
5 “ “ “ 60° to 70° C.....	20	250	79.8	80.1	+0.3
5 “ “ “ 60° to 70° C.....	50	650	79.8	78.9	-0.9
5 “ “ “ 60° to 70° C.....	50	650	79.8	79.3	-0.5
I “ “ “ 60° to 70° C.....	20	250	39.9	39.3	-0.6
I “ “ “ 60° to 70° C.....	20	250	79.8	79.2	-0.6
I “ “ “ 60° to 70° C.....	20	250	79.8	78.8	-1.0
I “ “ “ 60° to 70° C.....	20	250	79.8	77.4	-2.1
I “ “ “ 60° to 70° C.....	20	250	79.8	79.2	-0.6
I “ “ “ 60° to 70° C.....	20	250	79.8	79.2	-0.6
5 “ (NH ₄) ₂ NO ₃ +0.02 per cent. (NH ₄) ₂ HPO ₄ .	20	250	79.8	80.9	+1.1
5 “ “ “ “ “ “	20	250	79.8	80.2	-0.4

employed ; and all precipitations were made in the presence of an excess of phosphoric acid.

An examination of the table shows that, of the wash solutions, 5 per cent. ammonium nitrate washing twenty times gives practically theoretical results. As many as 50 washings with this solution give results slightly low but still good. The other solutions were rejected as they showed a decided solvent effect, except the ammonium nitrates plus ammonium phosphate, upon prolonged washing. Twenty washings were required to free the precipitate from chlorides, sulfates, and ammonium phosphate. In all succeeding work 5 per cent. ammonium nitrate was used, washing twenty times unless otherwise stated. Long heating with the blast, ten to twenty minutes, was required to reduce to constant weight.

Composition of the Ignited Aluminum Phosphate.—The phosphoric acid, in the aluminum phosphate washed twenty times with 5 per cent. ammonium nitrate, was carefully determined by precipitation with molybdate solution, washing the precipitate of ammonium phosphomolybdate with dilute nitric acid, and washing the final precipitate free of chlorides.

	Theory. P ₂ O ₅ . Mgs.	Found. P ₂ O ₅ . Mgs.
<i>a</i>	58.2	58.8
<i>b</i>	58.7
<i>c</i>	58.8
		Average, 58.8

The salt obtained under the above-mentioned conditions seems to be the normal phosphate, AlPO₄.

THE EFFECT OF THE PRESENCE OF SALTS OF SOME OTHER METALS.

Effect of Iron Salts.—Five grams of ammonium ferric alum dissolved in water, 2 grams of ammonium phosphate added, and treated as for aluminum phosphate, washing twenty times with ammonium nitrate, gave :

	Calculated as alumina. y
<i>a</i>	4.5
<i>b</i>	0.0
<i>c</i>	1.3
<i>d</i>	0.0

Precipitated while slightly warm.

Another series precipitated twice gave :

	Calculated as alumina. Mg.
<i>a</i>	0.4
<i>b</i>	0.0
<i>c</i>	0.0
<i>d</i>	0.0

Solutions containing aluminum sulphate, ammonium phosphate, and 5 grams of ammonium ferric alum precipitated once with ammonium thiosulphate, gave :

	Theory. Mgs.	Al ₂ O ₃ found. Mgs.
<i>a</i>	78.9	86.4
<i>b</i>	23.9	28.2

Both contained iron.

Similar solutions precipitated twice with sodium thiosulphate, gave :

	Theory. Mgs.	Al ₂ O ₃ found. Mgs.
<i>a</i>	39.9	39.4
<i>b</i>	39.9	40.8

These precipitates contained no iron.

Therefore, in the presence of large quantities of ferric iron, two precipitations only are necessary to separate the iron.

Effect of Calcium Salts.—Two grams of calcium phosphate, precipitated once, gave :

a, Nothing.

b, “

Aluminum phosphate plus 2 grams calcium phosphate, precipitated once, gave :

	Theory. Mgs.	Al ₂ O ₃ found. Mgs.
<i>a</i>	79.8	80.1
<i>b</i>	79.8	80.8
<i>c</i>	79.8	81.0
<i>d</i>	23.9	24.3
<i>e</i>	79.8	80.2
<i>f</i>	79.8	79.3

a, *b*, *c*, and *d* were washed twenty times with 5 per cent. ammonium nitrate; *e* and *f* were washed fifty times.

The error produced by the presence of calcium salts alone is

not so great as that produced by iron salts. In this case it seems probable that the error is produced by the well-known property of the aluminum precipitates of carrying down other salts mechanically. Two precipitations separate completely aluminum phosphate from very large quantities of iron and of lime, as is shown by the following data :

$\text{Al}_2(\text{SO}_4)_3$ Gram.	$\text{Ca}_3(\text{PO}_4)_2$ Gram.	$\text{NH}_4\text{Fe}(\text{SO}_4)_2$ Gram.	Al_2O_3 Theory. Mgs.	Al_2O_3 Recovered. Mgs.
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	39.9	39.6
$\frac{1}{5}$	$\frac{1}{2}$	$\frac{1}{4}$	19.9	18.8
$\frac{1}{8}$	$\frac{1}{2}$	$\frac{1}{4}$	19.9	18.8
$\frac{1}{4}$	2	I iron	39.9	39.7
$\frac{1}{4}$	2	I "	39.9	39.9

From the foregoing results the conclusion seems warranted that aluminum phosphate can be quantitatively separated by a soluble thiosulphate and ammonium chloride from a hydrochloric acid solution of iron, alumina, and lime phosphates containing only a small amount of sulphates. The statement of many observers, that theoretical results on aluminum phosphates can only be obtained in the presence of an excess of phosphoric acid, has been confirmed by my own work. The error produced by precipitating a second time without adding phosphoric acid amounted in some cases to 2 mgs. alumina.

The Effect of Magnesium, Sodium, and Potassium Salts.—Three solutions containing in 50 cc. the following :

	A. Gram.	B. Gram.	C. Gram.
Calcium phosphate.....	0.8000	0.7000
Calcium chloride.....	0.250
Magnesium chloride.....	0.0200	0.0100	0.0250
Potassium chloride.....	0.0100
Sodium chloride.....	0.0100
Iron	0.0185	0.0421	0.0125
Sodium hydrogen phosphate	2.0000
Aluminum sulphate.....	0.3504	0.1504	0.1000

gave

	A.		B.		C.	
	Theory. Mgs.	Found. Mgs.	Theory. Mgs.	Found. Mgs.	Theory. Mgs.	Found. Mgs.
Alumina	56.0	54.5	24.0	24.2	16.0	15.8
	56.0	56.3	24.0	23.9	16.0	15.8

The above-named salts therefore exert no disturbing influence on the accuracy of the final results.

The Effect of Silica.—It is stated by Carnot¹ that “ In the presence of silica the precipitate of aluminum phosphate contains a little silica.” I have tried to remove this silica by two precipitations but have failed, the plus error equivalent to Al_2O_3 being,

	Mgs.
<i>a</i>	1.2
<i>b</i>	0.6
<i>c</i>	3.3
<i>d</i>	2.5

In order to secure correct results, therefore, the silica must be removed from the mixture before the separation of the aluminum phosphate.

The Effect of Sulphates.—Removal of silica being a necessary operation it was determined to make the separation by the well-known method based on the insolubility of silica in sulphuric acid. This method, worked out very carefully by Drown,² is a very rapid and accurate process, which is used almost exclusively in the determination of silica in pig-iron. Essentially the same method has been worked out and used by others for the determination of silica in furnace products.

While the separation of silica by this method is all that can be desired it was found to be impossible to completely precipitate the aluminum phosphate with a thiosulphate in the filtrate.

From solutions containing various quantities of the sulphates, phosphates, and chlorides of iron, aluminum, and lime, the following results were obtained :

Experiment.	H_2SO_4 present. Grams.		Alumina.	
			Theory. Mgs.	Found. Mgs.
2	0.100	1 precipitation	39.9	39.8
11	0.20	1 “	79.8	79.6
12	0.20	1 “	80.1
19	0.20	1 “	80.1
20	0.20	1 “	80.8
20a	0.10	1 “	23.9	24.2
33a	1.250	2 “	39.9	39.6
34a	1.250	2 “	40.7

¹ Blair's "Chemical Analysis of Iron," p. 188.

² *J. Inst. Min. Eng.*, 7, 34c.

Experiment.	H ₂ SO ₄ present. Grams.			Alumina.	
				Theory. Mgs.	Found. Mgs.
50	2.800	2	"	38.7
35a	7.500	2	"	19.9	16.8
36a	7.500	2	"	18.7
39c	7.500	2	"	39.9	37.9
39d	7.500	2	"	37.8
38a	36.000	1	"	31.9	17.2

The presence of more than 1.25 grams of sulphuric acid prevents the complete precipitation of aluminum phosphate, while 2.75 grams give a decided error. The presence of ammonium acetate did not give any better result; see result marked "Experiment 50."

The Effect of Fluorine.—The presence of a fluoride in a solution from which it is attempted to separate aluminum by this method is as disastrous to the results as is the presence of sulphates. From solutions containing phosphates, chloride, and small amounts of sulphates of aluminum, iron, magnesia, lime and soda, and fluoride, the results below are obtained:

		Fluorine present. Mgs.	Alumina.	
			Theory. Mgs.	Found. Mgs.
a	2 precipitation	50	39.9	28.4
b	2 "	50	27.4
c	2 "	50	19.9	8.9
d	1 "	250	36.9	31.6
e	2 "	250	28.5
f	2 " 1st 10 cc. CH ₃ COONa		25.3
g	2 " " " "		19.9	14.9
h	2 " " " "		39.9	31.0
i	2 " " " "		19.9	16.6

In none of the current methods is the presence of fluorine mentioned as a disturbing factor. Several determinations by the acetate method, both single and double precipitation in the presence of dissolved calcium fluoride, showed that it has no effect.

Experiment.	CaF ₂ present. Mgs.	Alumina.	
		Theory. Mgs.	Found. Mgs.
60a	250	89.9	40.9
60b	250	...	38.1
60c	125	19.9	19.4
60d	125	...	19.8

The Effect of Manganese, with solutions containing :

	Gram.
Aluminum sulphate	0.25
Calcium phosphate	0.5
Ammonium ferrous alum	0.25
Magnesium chloride.....	0.10
Manganese chloride	0.10

The following data were obtained :

Experiment.	Alumina.	
	Theory. Mgs.	Found. Mgs.
64a	39.9	40.5
64b	40.3

The work so far done shows that alumina can be quantitatively separated as phosphate from a hydrochloric acid solution containing aluminum, iron, manganese, lime, magnesium, sodium, and potassium, when only small quantities of sulphate are present, and that the presence of silica in the solution produces a plus error too large to be neglected, and that the presence of large quantities of sulphates or the presence of fluorides prevents the complete precipitation of aluminum phosphate. Therefore, to obtain accurate results, silica and fluorine must be removed while sulphates, not more than the equivalent of 1.25 grams of sulphuric acid, may be present.

The following method for alumina in phosphates is based upon the results of these experiments: Treat 1 gram of substance in a platinum dish with from 5 to 10 cc. hydrofluoric acid, let stand in the cold from two to three hours, heat on the water-bath to complete dryness, add 2 cc. concentrated sulphuric acid, running well around the sides, and heat at a low temperature until the substance no longer flows in the dish. By this process fluorine is completely expelled. Cool and add from 10 to 20 cc. concentrated hydrochloric acid, and warm a few minutes to soften the mass; transfer to a small beaker, and boil until all aluminum compounds are surely dissolved (fifteen to thirty minutes); filter from undissolved residue, if any, washing the filter thoroughly, add 50 cc. 25 per cent. ammonium chloride solution and ammonia until alkaline, then hydrochloric acid until the precipitate just dissolves. Cool, dilute to about 250 cc., and add 50 per

cent. sodium thiosulphate solution, drop by drop, until the solution is colorless, adding in all 20 cc.; cover with a watch-glass, boil half an hour, filter, wash back into the same beaker, and dissolve in boiling hydrochloric acid; reprecipitate exactly as before, after adding 2 cc. of a 10 per cent. ammonium phosphate solution. Wash twenty times with 5 per cent. ammonium nitrate solution, and ignite to constant weight. For the second precipitation ammonium thiosulphate may also be used but it is not strictly necessary.

According to the above method from solutions containing :

	Mgs.
Aluminum sulphate.....	250
Calcium phosphate.....	500
Ammonium ferrous alum.....	250
Silica	100
Calcium fluoride	100
Manganese chloride	100
Magnesium chloride.....	100

These results recorded below were obtained :

Experiment.	Alumina.	
	Theory. Mgs.	Found. Mgs.
63 <i>a</i>	39.9	40.0
63 <i>b</i>	39.5
63 <i>c</i>	40.1
63 <i>d</i> (contained fluorine)	37.8
63 <i>e</i>	19.9	19.6
63 <i>f</i>	20.3
65 <i>a</i>	39.9	39.5
65 <i>b</i>	39.9
66 <i>a</i> No. 1 ground S. C. rock	17.0 by acetate method	18.4
66 <i>b</i>	17.8
67 <i>a</i> " 4 " Florida	19.4 " " "	16.3
67 <i>b</i>	14.3

Move the decimal one place to the left to express percentages.

The phosphoric acid was determined in the aluminum phosphate obtained in Experiment No. 63.

	Theory. Mgs.	Found. Mgs.
<i>a</i>	58.2	58.0
<i>b</i>	57.6
<i>c</i>	57.2

Here, also, the phosphate seems to be the normal, AlPO_4 , although it was separated in the presence of all substances likely to be found in a natural phosphate, with the exception of silica and fluorine.

The greatest difficulty to be overcome in the execution of this method is the error produced by the presence of fluorine; hence it is necessary to heat the substance for a long time with sulphuric acid to insure the complete removal of fluorine before beginning the separation of the aluminium phosphate.

An attempt to overcome this source of error by adding an alkaline acetate before boiling with thiosulphate gave no better result. In one experiment, however, in which the acetate was added after the boiling, and ten minutes before filtering, all the aluminium phosphate was removed.

The determination of ferric oxide was made as follows: Dissolve 1 gram of substance in 20 cc. sulphuric acid, dilute, filter, washing the filter thoroughly, and if any organic matter is present add a little potassium chlorate and boil until chlorine is expelled. Reduce with zinc, filter, and titrate at once with potassium permanganate solution, 1 cc. of which equals 0.0025 gram ferric oxide.

From solutions used in Experiment 63 I obtained:

	Ferric oxide.	
	Theory. Mgs.	Found. Mgs.
<i>a</i>	51.8	52.5
<i>b</i>	52.2
<i>c</i>	52.2
<i>d</i>	52.2
<i>e</i>	51.7
<i>f</i>	51.4
No. 1 ground S. C. rock ..	30.6 by acetate method	29.4
.....	29.3
“ 4 “ Florida “ ..	14.5	15.4
.....	15.1

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