No. 5.—Length, 82 mm., diameter, 3.43 mm. Resistance at 20° = 2.48 legal ohms. Specific resistance = 279.4.

This specimen was a piece of No. 4 after a portion had been broken off.

No. 6.—Length, 84.5 mm., diameter, 3.05 mm. Resistance at 20° = 5.88 legal ohms. Specific resistance = 508.3.

No. 7.—Length, 86.1 mm., diameter, 4.83 mm. Resistance at 20° = 5.37 legal ohms. Specific resistance = 1152.

On close examination this bar was found to be cracked.

No. 8.—Length, 57.5 mm., diameter, 2.92. Resistance at 20° = 4.68 legal ohms. Specific resistance = 544.5.

As all of the bars showed a strong cleavage on the ends, the measurements could only be approximate, and when they are calculated to the standard conditions, one meter in length, with a cross section of one mm., the errors of measurement are correspondingly multiplied.

By using an ordinary copper clamp contact, almost any resistance can be obtained according to the amount of pressure exerted by the clamp; no difference in resistance could be detected when working in the light or dark.

By comparison of the results obtained, it will be observed that the mean would be about 500; however, from the great tendency to crystallization that the metal shows, it would seem more probable that the lowest result more nearly approaches the true figure. As gas carbon has a specific resistance equal to 50, the resistance of tellurium is seen to be enormous. The result obtained by Matthieson,[1] 0.000777 for the conductivity compared with silver as 100, would give a specific resistance of more than 2000, showing that the structure of his metal must have been different from ours or that different contact was made.

THE VOLUMETRIC DETERMINATION OF MAGNESIA.

BY JAMES OTIS HANDY.

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EVERY chemist, who has to make many determinations of magnesia in water, cement or other material, appreciates the difficulties surrounding the gravimetric process. These difficulties chiefly arise from the fact that the change from magne-

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[1] *Pogg. Ann.*, 103, 428.

sium ammonium phosphate to the pyrophosphate of magnesia is attended by a rapid consolidation or sintering of the mass. By this means particles of carbon from the filter-paper are often firmly enclosed in the lumps of precipitate.

If gradual heating over a Bunsen burner is continued long enough, fifteen minutes over the blast-lamp with crucible inclined and cover placed in a position to facilitate oxidation, will give a pure white pyrophosphate. If, however, the preliminary heating proceeds too rapidly, or is not continued long enough before applying the blast, it is almost impossible to burn off all the carbon.

The method recommended by Fresenius for completing the oxidation of such material by treatment with nitric acid followed by evaporation and re-ignition, yields a pure white residue, but the result is invariably low. The author found that pure magnesium pyrophosphate when so treated lost weight every time, although no mechanical loss took place. Moreover, repetition of the treatment caused further serious loss. Constant weight was not reached.

No one who has adopted the volumetric method for determining calcium oxalate by means of standard permanganate would ever go back to the gravimetric way. When a simple and accurate method for the volumetric determination of magnesia appears, it will be equally useful.

The alkalimetric method published by Stolba in 1866[1], referred to by Sutton, Hart, Meade[2] and others, has not come into general use. The reaction is:

$$MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4.$$

Its unpopularity is doubtless due to the use of alcohol for removing the ammonia wash from the magnesium ammonium phosphate precipitate, it being an expensive and tedious procedure.

Meade proposes a radical change from the usual phosphate method. He estimates the magnesia by precipitating it as arsenate and determines by standard thiosulphate the amount of iodine which a hydrochloric acid solution of the precipitated arsenate liberates from potassium iodide. The procedure seems

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[1] *Chem. Centrbl.*, 728 (1866).

[2] This Journal, 21, 746 (1899).

rapid and accurate, but it would appeal only to those who prefer an iodometric to an alkalimetric method.

The writer has endeavored to eliminate the objectionable feature of Stolba's method by discarding alcohol and removing the free ammonia from the phosphate precipitate by taking advantage of the volatility of ammonia.

It was necessary to find some way of expelling the ammonia without in any way affecting the integrity of the phosphate which should remain. In view of the fact that Fresenius, Roscoe and Schorlemmer, and other authorities all agree that the only change which $MgNH_4PO_4.6H_2O$ suffers at 100° C., is the loss of 5 molecules of water of crystallization, it seemed a simple thing to put filter and precipitate into 50 cc. of distilled water, and after removing the ammonia by boiling down to 30 cc., to cool, add a measured excess of standard acid to dissolve the precipitate, and then to titrate back with standard alkali. After many trials in which the results were all low and irregular this method was abandoned. Evidently some change of composition took place at 100° C. under these conditions.

Other means of subjecting the ammoniacal precipitate to this temperature were tried. The filters containing the precipitates were spread out flat on strong 5-inch filters, and were placed, one set at a time, in a funnel through which a current of steam was rising, and allowed to remain for ten minutes. The ammonia was expelled, but the results by titration were still low, although absolutely no mechanical loss or loss by solution took place. There was a loss in alkalinity due to a chemical change other than the loss of water of crystallization.

Thinking that the presence of water in the one, and of steam in the other of these experiments, might have brought about a change which temperature alone could not have accomplished, a set of experiments were made wherein the filters and precipitates were dried in an oven at 100° C., away from all but the moisture which they at first contained. By this means also, low results were obtained.

It was then apparent that no rapid or satisfactory method could be based on titration of magnesium ammonium phosphate which had been dried at 100° C., or even heated to that temperature without drying. Although the change in alkalinity might be perfectly definite and complete, it would require much longer for large precipitates to be completely transformed than for small ones, and irregular results would surely be obtained.

Before rejecting the statement of such eminent authorities with regard to the effect of drying magnesium ammonium phosphate at 100° C., it was thought best to completely eliminate the moisture element from the experiment.

A quantity of the pure salt was prepared by precipitation under standard conditions from a solution of magnesium chloride. After washing thoroughly with 10 per cent. ammonia wash (1 part of ammonium hydroxide, sp. gr. 0.90, mixed with 9 parts of water), the precipitate was spread out on filter-paper and allowed to dry in the air. It was then dried over sulphuric acid, after which it was ground, mixed and placed in a stoppered bottle. Weighed portions were then tested for purity, and this having been established, the property in question was examined into.

PROPERTIES OF $MgNH_4PO_4.6H_2O$.

	Statement of authorities. Per cent.	Actual facts. Per cent.
Loss of weight at 100° C. (water, etc.)	36.70	41.43
Yield of $Mg_2P_2O_7$ on ignition	45.34	45.59
Cc. $\frac{N}{10}$ H_2SO_4 for 1 gram before 100° drying	82.05	81.94
The same if dried at 100° C. beforehand	82.05	54.59
Loss of original alkalinity at 100° C. (per cent.)	00.00	33.38

The author does not wish to be understood as saying that the first column in the above table represents verbatim the statements of Fresenius and others, but that it does represent the exact results which would follow if their statements were true.

By comparing the magnesium oxide value of decinormal sulphuric acid when used on air-dried $MgNH_4PO_4.6H_2O$ with the value when a weighed amount of the same salt is heated to constant weight at 100° C. before titration, it will be seen that the difference is very great.

1 cc. $\frac{N}{10}$ $H_2SO_4 = 0.002$ gram MgO in the air-dried salt.

1 cc. $\frac{N}{10}$ $H_2SO_4 = 0.003$ gram MgO in the same material if first dried at 100° C.

Although the definiteness of this change is now firmly established, the formula of the compound which is formed at 100° C., has not yet been determined.

The folly of drying at 100° C. as a preliminary to the titration of $MgNH_4PO_4.6H_2O$ having been established, the author determined to ascertain the speed with which ammonia evaporated from phosphate precipitates at ordinary temperature. It was found that if filters containing precipitates were opened flat after washing, and placed face upward on heavy dry filter-paper of the sort made by Whitall, Tatum & Co., for druggist's use, the bulk of the moisture would be drawn out in a few minutes, and if transferred then to a second dry paper and allowed to stand for half an hour to one hour, the ammonia, so far as its power of neutralizing a measurable quantity of acid was concerned, had entirely disappeared. When the filter-papers have become dry for a distance equal to one-fifth of the diameter of the paper, measured from the outer rim, it is certain that the ammonia has been expelled. This is, of course, based on the assumption that the precipitate is distributed fairly evenly over the rest of the paper.

Methyl orange was the indicator used, and in all cases a clear yellow was considered the end-point when using decinormal sodium hydroxide to measure the excess of decinormal sulphuric acid.

Titration of $MgNH_4PO_4.6H_2O$.

	Time for precipitation.		Time of drying,		Temperature.	MgO used.	MgO found.	Error.
	Hrs.	Min.	Hrs.	Min.		Gram.	Gram.	Gram.
1	3	0	18	6	21° C	0.00475	0.00478	0.00003
2	3	0	18	6		0.01900	0.01900	0.00000
3	3	0	18	6		0.02375	0.02377	0.00002
4	3	0	18	6		0.04750	0.04785	0.00035
5	1	30	2	0	19	0.02375	0.02377	0.00002
6	1	30	2	30	19	0.02375	0.02377	0.00002
7	1	30	3	0	19	0.02375	0.02377	0.00002
8	1	30	3	20	19	0.02375	0.02377	0.00002
9	1	30	2	0	19	0.02375	0.02377	0.00002
10	1	30	1	0	19	0.02375	0.02377	0.00002
11	1	30	1	0	21	0.04750	0.04775	0.00025
12	1	30	1	30	21	0.01907	0.01990	0.00083
13	1	30	1	30	21	0.01907	0.01930	0.00023
14	1	30			21	0.03814	0.03830	0.00016
15	1	30	1	30	21	0.05720	0.05740	0.00020
16	1	30	1		21	0.05720	0.05780	0.00060
17	1	30		30	21	0.01907	0.01920	0.00013
18	1	30		30	21	0.01907	0.01920	0.00013

	Time for precipitation.		Time of drying.		Temperature.	MgO used. Gram.	MgO found. Gram.	Error. Gram.
	Hrs.	Min.	Hrs.	Min.				
19	1	30	0	45	21	0.03814	0.03830	0.00016
20	1	30	1	15	21	0.03814	0.03800	0.00014
21	1	30	1	0	21	0.05720	0.05670	0.00050
22	1	30	1	0	21	0.05720	0.05680	0.00040
23	1	30	0	25	65	unknown	0.05650	
24	1	30	0	25	65	unknown	0.05650	
25	1	30	1	15	21	unknown	0.05650	
26	1	0	1	0	21	0.04767	0.04711	0.00056
27	1	0	0	20	59	0.04767	0.04771	0.00004
28	1	0	0	40	62 av. 66 max.	0.04767	0.04671	0.00096
29	1	0	1	0	62 av. 66 max.	0.04767	0.04631	0.00136
30	5 shaking 30 standing			60	21	0.00095	0.00090	0.00005
31	5 shaking 45 standing			60	21	0.00048	0.00050	0.00002

Experiments like the above prove the accuracy of the alkalimetric method for magnesia determination. The cases of significant error in the table may be divided into those caused by imperfect removal of the ammonia (Nos. 12 and 16); those caused by drying too long and at too high a temperature in the oven (Nos. 28 and 29); those doubtless caused by imperfect manipulation (Nos. 21, 22, and 26); and, finally, those inherent in the process itself. The latter are all very small if, indeed, they exist at all. Experiments 23, 24, and 25 are comparative only.

Experiments Nos. 30 and 31 show not only the extreme delicacy of the reaction on which the method depends, but they show how rapid the reaction is, even in very dilute solutions, and how insoluble the phosphate is in 10 per cent. ammonia wash.

It was found that five minutes' shaking in a stoppered flask at ordinary temperature sufficed, if followed by fifteen minutes' standing, to completely precipitate any magnesia solution containing as much as 0.002 gram of magnesium oxide in 100 cc. With amounts exceeding 0.05 gram per 100 cc., it is believed that filtration could be begun in five minutes after the end of the shaking process.

In order to ascertain what temperature could be safely used to expedite the expulsion of ammonia from the phosphate precipitates, a series of experiments were made. It was found that at 55° C. there was no appreciable loss of alkalinity but that at 65° a loss of 1 per cent. had taken place. Several experiments in which the filters and precipitates were removed from the oven as soon as the outer half-inch of the papers were dry, gave identical results with air-drying at 21° C. From fifteen to thirty minutes in the oven at 50° to 60° C. suffices. If the drying of the precipitate proceeds too far, solution in decinormal sulphuric acid is slow. If, however, the drying is stopped at the point described there is enough moisture left so that, on stirring, the precipitate blends quickly with the acid and soon dissolves.

For the drying a large, rectangular, double-walled oven of the kind sold with oil or gas stoves is cheap and convenient.

Unless magnesia determinations are constantly being made, it will often be more convenient to let the precipitates air-dry than to use an oven.

The tendency of magnesia to precipitate with iron and alumina and with calcium oxalate must be met by re-solution in hydrochloric acid and reprecipitation. When the amount of lime is considerable, it is best to burn off the first oxalate precipitate before dissolving in hydrochloric acid. By this means the oxalate is decomposed and the addition of ammonia alone does not cause its sudden reprecipitation. Even in the second precipitation, if the boiling is allowed to proceed longer than is necessary to make the finely crystalline calcium oxalate settle well, some magnesium oxalate is sure to precipitate, betraying its presence by its coarser texture. The solution for magnesia precipitation usually does and always should contain in the form of ammonium chloride the equivalent of 5 cc. of concentrated hydrochloric acid per 100 cc.

THE METHOD.

Add ammonia (sp. gr. 0.90), equivalent to one-tenth of the solution. Cool in water to 20° to 25° C. Precipitate by adding slowly with constant stirring a saturated solution of sodium ammonium phosphate, using 1 cc. for each 0.01 gram magnesium oxide. Stir vigorously for about five minutes or shake in a flask for an equal length of time. In the former case let the solution stand until the clarification of the upper liquid shows that the reaction is complete. In the case of flask precipitations, if over 0.002 gram of magnesium oxide is present the solution may be filtered in fifteen minutes. Suction may be used if desired but if many solutions are to be filtered at once little is gained by its use. Use 10 per cent. ammonia wash (one part ammonia (sp. gr. 0.90) to nine of water). Deliver it preferably from an aspirator bottle placed about 4 feet above the bench. Wash by decantation as far as possible. Finally wash the precipitate which has gone on the filter, back into the beaker, stir it up with the ammonia wash and bring it again completely on the filter-paper. Wash once more, leaving the upper edge of the filter clear of precipitate so that it can be handled. Avoid assembling all of the precipitate in the apex but leave it fairly evenly distributed over the lower two-thirds of the paper. Allow the precipitates to drain and then transfer each in turn to a dry 5-inch filter-paper, allowing them to remain there open and face upward until the bulk of the moisture has been absorbed. After about three minutes transfer them to fresh dry filters, and in the case of heavy precipitates to a third set a few minutes later. Then place the filters on a shelf to dry at the temperature of the room or place filter-papers and backing on the grating of an air oven having a temperature of 50° to 60° C. After fifteen or twenty minutes in the oven or forty-five minutes in the air, watch for the time when the filters have dried inward half an inch from the margin. This appearance has been found to indicate that the evaporation has gone far enough to insure the expulsion of the free ammonia. The precipitates and filters may then be removed and placed in small dry beakers where they are treated each with a measured excess of decinormal sulphuric acid, and stirred until the papers are disintegrated and the precipitates dissolved. Two drops of a 0.1 per cent. alcoholic solution of methyl orange are then added. If this gives a clear decided pink, enough acid has been added. If it is only faintly pink the excess of acid is slight and some minute particles may have escaped solution. In such cases add five cc. more decinormal sulphuric acid and stir well. Finally dilute to about 100 cc. and titrate back with decinormal sodium hydroxide solution to the appearance of a clear yellow color, free from all suggestion of pink.

$$1 \text{ cc. } \tfrac{N}{10}\ H_2SO_4 = 0.002 \text{ gram MgO.}$$

If filtrations have taken place during the latter part of the day the filters may be removed from the funnels and allowed to stand over night after which they are titrated as described.

The writer hopes that the simplicity and accuracy of the method may render it generally useful.

PITTSBURG, December 25, 1899.

A PRELIMINARY COMMUNICATION UPON RICININE.

BY THOMAS EVANS.

Received January 2, 1900.

TUSON[1] obtained a substance crystallizing in plates which he called ricinine, by extracting castor beans, the seed of the *Ricinus communis*, with boiling water, filtering, evaporating to a thick sirup and again extracting with boiling alcohol.

Tuson states that ricinine is soluble in water and alcohol and very little soluble in ether and benzene, and that when heated with solid potassium hydroxide ricinine evolves ammonia.

He describes, but gives no analyses of crystalline compounds obtained by the action of nitric acid, mercuric chloride, and platinic chloride.

No salts with acids, with the possible exception of the nitric acid salt, were obtained by Tuson.

A few years later Werner[2] claimed that the ricinine of Tuson contained no nitrogen and was the magnesium salt of an acid with the formula $C_{11}H_{20}O_{10}Mg_2.2H_2O$. To this Tuson[3] replied that Werner had evidently investigated an entirely different substance, as his ricinine contained 20.79 per cent. of nitrogen.

Schulze[4] obtained a nitrogenous substance from the germinated seed of *Ricinus communis*, by extracting with alcohol, distilling this off, taking up the residue with water, treating with tannic acid and lead acetate, filtering, removing lead with hydrogen sulphide, and evaporating the filtrate to small bulk.

The impure product was purified by boiling the aqueous solution with animal charcoal and finally by crystallizing from absolute alcohol, from which it separated in small colorless prisms melting at 193° C.

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[1] *J. Chem. Soc.*, 17, 195.

[2] *Jsb. d. Chem.*, 877 (1870).

[3] *Ibid.*, 877 (1870).

[4] *Ber. d. chem. Ges.*, 30, 2197.