

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.¹

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ONE of the elements for which, so far, no satisfactory volumetric method of determination, of general application, has been found, is magnesium. Stolba² suggested a volumetric method depending upon the fact that one molecule of magnesium ammonium phosphate required two molecules of mineral acid for solution. Hart and Sutton both describe the method in detail, in their works upon volumetric analysis, and call attention to its accuracy. Hartzell, a student in the laboratory of Lafayette College, in his thesis work for graduation, in 1897, made use of the method in determining magnesia in cement and the result of his investigations, also, showed the method to be fairly accurate. The great objection to Stolba's method, particularly if it is resorted to as a time-saver, is the tedious washing of the precipitated magnesia with alcohol, in order to get rid of the ammonia, making the volumetric determination very little if any quicker than the gravimetric. In any event, so far as I know, the method is very little if ever used even in commercial laboratories where magnesia determinations are a part of the daily routine.

Analogous to the phosphates are the arsenates. If instead of adding sodium phosphate to an ammoniacal solution containing magnesium we add sodium arsenate, magnesium ammonium arsenate, corresponding to magnesium ammonium phosphate, is precipitated. This reaction is of course a familiar one, since it is the one upon which the usual gravimetric determination of arsenic is based. Now if the magnesium in a solution can be entirely precipitated as a double arsenate of magnesium and ammonium, if the magnesium and arsenic in this compound bear a fixed ratio to each other, if the precipitate can be collected and washed free from sodium arsenate, then clearly any volumetric method which will give us the weight of arsenic in the precipitate

¹ Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899.

² *Chem. Centrbl.* (1866), 728.

will also tell us indirectly the amount of magnesium in the solution. From the formula of the double salt, $Mg_2(NH_4)_2As_2O_8 \cdot H_2O$, it will be seen that one atom of magnesium is equivalent to one atom of arsenic and consequently the ratio between the magnesium and arsenic is 24.28 : 75.01.

As the first step looking to the formulation of a volumetric method along these lines, a stock solution of magnesium was prepared as follows: Fifty grams of pure magnesium chloride were dissolved in about 700 cc. of water and a little ammonium oxalate added to precipitate any traces of calcium present. The solution was allowed to stand for a day when the very slight precipitate of calcium oxalate was filtered off. A sufficient quantity of ammonium oxalate to convert all the magnesium in the solution to magnesium oxalate was next added and the solution evaporated to small bulk over a water-bath. The separated magnesium oxalate was collected, washed, dried, and ignited, first at a low temperature and then at a higher until finally at a red heat. Of the pure magnesium thus obtained, five grams were dissolved in dilute hydrochloric acid and the solution diluted to two liters. Each fifty cc. of this solution should have been equivalent to 0.2500 gram of magnesium oxide. Checked by precipitation with sodium phosphate, fifty cc. gave:

I. 0.6900 gram of $Mg_3P_2O_7$ equivalent to 0.2497 gram of MgO .

II. 0.6891 gram of $Mg_3P_2O_7$ equivalent to 0.2493 gram of MgO .

Checked by evaporation to dryness and ignition of the residue, fifty cc. gave:

0.2490 gram of MgO .

0.2498 gram of MgO .

The average of the four determinations is 0.2495 gram MgO .

A search into the literature on the solubility of the magnesium ammonium arsenate showed the precipitate to be less soluble where an excess of sodium arsenate was present in the ammoniacal solution; accordingly, wherever the magnesium was precipitated by sodium arsenate, a considerable excess of the precipitant was used. The precipitate of course must be washed with dilute ammonia water and, as it is not entirely insoluble in this medium, the volume of the washing fluid should be kept as small as possible.

Following these points, fifty cc. of the stock solution were diluted to 500 cc. and 50 cc. of sodium arsenate (ten per cent.) solution added; then ammonia, drop by drop, with constant stirring until the precipitate began to form. At this point the addition of ammonia was interrupted and the solution stirred for five minutes after which one sixth the volume of the solution of strong ammonia was added and the mixture stirred for five minutes longer and allowed to stand over night. In the morning the precipitated magnesium ammonium arsenate was collected in a Gooch crucible, dried, and ignited at a very low temperature and weighed as magnesium pyroarsenate, containing 25.94 per cent. of magnesium oxide. The results were:

No.	Mg ₃ As ₂ O ₇ Gram.	Equivalent to MgO. Gram.
1	0.9599	0.2490
2	0.9545	0.2476
3	0.9592	0.2488
4	0.9573	0.2483
Average		0.2484
Instead of		0.2495
Difference		0.0009

As a further test the magnesia from fifty cc. of the stock solution was precipitated as described, dissolved in dilute hydrochloric acid and the arsenic thrown out of solution with hydrogen sulphide. The magnesium remaining, was then determined as pyrophosphate with the following results:

No.	Mg ₂ P ₂ O ₇ Gram.	Equivalent to MgO. Gram.
1	0.6883	0.2490
2	0.6865	0.2484
3	0.6870	0.2486
Average		0.2487
Instead of		0.2495
Difference		0.0008

In the same manner, the magnesium in fifty cc. of the stock solution was precipitated as magnesium ammonium arsenate, dissolved in hydrochloric acid and the arsenic determined as magnesium pyroarsenate by addition of magnesia mixture. The results were:

No.	Mg ₃ As ₂ O ₇ . Gram.	Equivalent to MgO. Gram.
1	0.9590	0.2488
2	0.9536	0.2474
3	0.9552	0.2478
Average		0.2481
Instead of		0.2495
Difference		0.0014

These three sets of results while a little low, showing that a slight loss of magnesia is incurred, probably due to solution of the precipitate in the mother-liquor and the wash-water, nevertheless, fall well within the limits of allowable variation for technical work, and show the ratio between the magnesium and arsenic to be constant.

The next step was to find a suitable volumetric method for determining the arsenic. This being in the state of arsenic acid excluded all methods supposing the element to be in the condition of lower oxidation. The methods of Pierce and McCay depending upon the precipitation of the arsenic as silver arsenate by an excess of standard silver nitrate and the determination of, either the silver in the precipitate or the excess of silver in the solution, by titration with sodium thiocyanate were also not considered, as both time and expense made them unsuitable for commercial work.

Of the methods depending upon the reduction of the arsenic to arsenious acid and the titration of the latter by standard iodine, that making use of the reaction between arsenic acid and potassium iodide in acid solutions offered the best field for investigation and following the method as laid down by Gooch and Browning,¹ several determinations were made. The process followed consisted in dissolving the precipitated arsenate in dilute sulphuric acid, adding an excess of potassium iodide and ten cc. of sulphuric acid (1 : 1) and diluting to 100 cc. The solution was boiled rapidly until the volume reached 40 cc. and the free iodine in the solution destroyed by careful addition of sulphurous acid (roughly made about one-half normal). Sodium carbonate was then added until the solution was nearly neutral and next an excess of sodium bicarbonate over what was required to make it so. The arsenious acid was then titrated with standard iodine

¹ *Am. J. Sci.* (3), 40, 66.

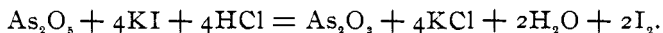
solution. This latter was made by dissolving 52.24 grams of pure resublimed iodine in a solution of 75 grams of potassium iodide in 200 cc. of water and diluting to one liter. Each cubic centimeter of this solution should be equivalent to 0.005 gram of magnesium oxide. The following satisfactory results were obtained by this method.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	Iodine required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.6	0.2480
2	50	0.2495	49.7	0.2485
3	25	0.1247	24.9	0.1245
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.9	0.0495
6	10	0.0499	10.0	0.0500

The time required to determine the arsenic by this method was from one-half to three-quarters of an hour.

The next, and the method finally adopted as the one most suited to the volumetric determination of magnesium, was the one worked out by A. Williamson and described by him in the *Journal of the Society of Dyers and Colourists*, May, 1896. A description of the method is also to be found in Sutton's "Volumetric Analysis," page 369.

It depends like the method of Gooch and Browning upon the reaction between arsenic acid and potassium iodide. Williamson found that where a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced from the higher to the lower state of oxidation, even in the cold, according to the reaction



For every molecule of arsenic acid reduced, corresponding to two atoms of magnesium, two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate and from the amount of standard solution required the magnesium calculated.

The process followed consisted in dissolving the precipitated magnesium ammonium arsenate in dilute hydrochloric acid, washing the filter-paper well with the acid and, after adding potassium iodide and allowing to stand for a few minutes, titrating with standard thiosulphate. This latter corresponded, cubic

centimeter for cubic centimeter, with the iodine solution mentioned above. Below are the results.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	"Hypo" required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.8	0.2490
2	50	0.2495	49.9	0.2495
3	25	0.1247	25.0	0.1250
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.95	0.0498
6	5	0.0249	5.0	0.0250

Determinations required only from seven to ten minutes by this method after the arsenic was in solution and were just as accurate as those by the longer method of digestion with potassium iodide.

The attempt was next made with success to hasten the precipitation of the magnesium by violent agitation. Fifty cc. of the stock solution were measured into a large Erlenmeyer flask, diluted to about 500 cc. and one-third this volume of strong ammonia and 50 cc. of a ten per cent. solution of sodium arsenate added, the flask corked up tightly and shaken violently by hand for ten minutes. After allowing the precipitate to settle, it was filtered and the arsenic determined as described above.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	"Hypo" required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.9	0.2495
2	50	0.2495	49.9	0.2495
3	25	0.1247	24.8	0.1240
4	15	0.0748	15.0	0.0750
5	10	0.0499	9.9	0.4950
6	5	0.0249	4.9	0.0245

The time required for the precipitation, filtration, washing, re-solution, and titration, had now been shortened to about three-quarters of an hour.

The standard thiosulphate was titrated against standard sodium arsenate, prepared by dissolving 12.29 grams of pure arsenious acid in nitric acid, evaporating to dryness on a water-bath, neutralizing with sodium carbonate and diluting to one liter. Each cc. of this solution was equivalent to 0.005 gram of magnesium oxide. The values obtained by titration of the standard thiosulphate against this solution coincided with those

obtained by titration with standard iodine solution. The values obtained by titration against standard bichromate and potassium iodide did not differ materially from those obtained by titration against standard arsenate or standard iodine.

The method finally worked out is as follows :

Pour the solution, which should not contain too great an excess of ammonium chloride or ammonium oxalate, into a large Erlenmeyer flask or a gas-bottle of sufficient capacity. Add one third the volume of the solution of strong ammonia and fifty cc. of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat, and wash with a mixture of three parts water and one part strong ammonia, until the washings cease to react for arsenic. Avoid using an excess of the washing fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1 : 1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 75 or 100 cc. Cool, if not already so and add from three to five grams of potassium iodide, free from iodate ; allow the solution to stand a few minutes and then run in the standard thiosulphate until the color of the liberated iodine fades to a pale straw color. Add starch and titrate until the blue color of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue color is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms which, however, dissolves when the thiosulphate is added.

Below are some results upon the method as given above :

Sample.	MgO. Gravimetric. Per cent.	Thiosulphate required. cc.	MgO. Volumetric. Per cent.
Dolomite	21.78	43.3	21.65
		43.4	21.70
Limestone	9.16	18.2	9.10
		18.2	9.10
Slag	16.42	32.6	16.30
		32.5	16.25
Cement, Portland	2.57	5.1	2.55
Cement, Natural	11.03	22.0	11.00
		22.2	11.10

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