issuing from the bed of the lake along its west shore line. One in particular has been explored which issues from a crater or sink 100 feet deep with a diameter of several hundred feet. The water delivered forms an important part of the present lake supply. A pipe lowered into the cavity caused the water to rise in the pipe above the lake surface. This water was too hot to permit coming in contact with the hands without seriously scalding or burning."

It is hoped that there will be an opportunity of securing the material necessary to make a comparison of the spring water with that of the lake.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 102.]

THE APPLICATION OF BISMUTH AMMONIUM MOLYBDATE TO GRAVIMETRIC ANALYSIS.[1]

BY EDMUND H. MILLER AND FREDERICK VAN DYKE CRUSER.

Received December 9, 1904.

BISMUTH may be determined volumetrically by the titration of reduced molybdenum from bismuth ammonium molybdate, which is precipitated in a barely acid solution by ammonium molybdate.[2] It was suggested by Dr. W. A. Noyes that the precipitate of bismuth ammonium molybdate might be ignited and the combined oxides weighed.

Therefore, this work was undertaken in order to determine whether this method could be made sufficiently accurate to be used as a method for the determination of bismuth, and to determine how it compares with the volumetric method.

EXPERIMENTAL.

A bismuth nitrate solution was made up, containing about 19 grams of the crystallized salt per liter, and 45 grams of free nitric acid; also a large amount of ammonium sulphate solution and ammonium nitrate solution (each 30 grams of the crystallized salt per liter). The bismuth nitrate solution was first standard-

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[1] Read at the meeting of the New York Section of the American Chemical Society, January 6, 1905.

[2] Riederer: This Journal, **25**, 907 (1903).

ized, and as the subsequent results depended upon the accuracy in the determination of the bismuth content of the solution, several methods were pursued in order to find the exact percentage of bismuth present.

First, different quantities of the bismuth solution were taken, a few drops of concentrated nitric acid added to each, and the solutions evaporated to dryness on the water-bath in weighed platinum milk dishes. These were then heated in an air-bath at 120° C., and finally ignited and weighed. It was noticed that the oxide was brown in color and that it melted. The results are given below:

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
15	0.1336	0.1198	0.007987
20	0.1783	0.1599	0.007995
20	0.1784	0.1600	0.007999
25	0.2225	0.1995	0.007984
30	0.2670	0.2394	0.007981
35	0.3127	0.2795	0.007987
		Average,	0.007989

Two of these residues were again dissolved in a few drops of nitric acid, evaporated to dryness at 160° C. in an air-bath, and heated in a muffle-furnace, giving slightly higher results.

The bismuth solution was next standardized by precipitating the bismuth as basic carbonate by the addition of ammonia and ammonium carbonate, and filtering on a platinum Gooch crucible, washing with cold water. When thoroughly washed, the precipitate was ignited to oxide and weighed, giving the following results:

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
15	0.1345	0.1206	0.008041
20	0.1791	0.1606	0.008031
		Average,	0.008036

Different amounts of the bismuth solution were precipitated by ammonia and ammonium carbonate as before, but filtered on ashless papers, dried, the precipitate separated from the paper, the paper moistened with nitric acid and burned in a weighed porcelain crucible, the bulk of the precipitate added and ignited to oxide with nitric acid.

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
15	0.1320	0.1184	0.007892
20	0.1746	0.1566	0.007829
25	0.2211	0.1983	0.007931
		Average,	0.007884

From these results we can readily see that some bismuth is lost, although the precipitates were treated very carefully.

The results obtained by weighing the ignited basic carbonate in a platinum Gooch crucible being somewhat higher than those obtained by evaporation and ignition in platinum, it was thought that these low results were due to a slight reduction by unburned gases, probably hydrogen, passing through the bottom of the platinum dish. Therefore, different amounts of the bismuth solution were evaporated to dryness in large porcelain crucibles, dried at 160° C. in an air-bath and ignited. The oxide obtained was canary-yellow in color.

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
20	0.1793	0.1608	0.008039
25	0.2238	0.2007	0.008028
30.025	0.2692	0.2414	0.008047
		Average,	0.008038

This value for bismuth corresponds with that obtained by the basic carbonate ignition in a platinum Gooch crucible, and, therefore, 0.008037 gram bismuth per cubic centimeter was taken as the correct value of the solution.

To find whether bismuth ammonium molybdate may be ignited and the bismuth thus determined from the oxides $Bi_2O_3.4MoO_3$, different quantities of the bismuth nitrate solution were precipitated according to the method of Riederer,[1] washing one series with ammonium sulphate and another with ammonium nitrate. The precipitates were filtered by suction on a platinum Gooch crucible, and washed with from 300 to 400 cc. of these solutions. When washed, the precipitates were dried by standing the crucibles on an asbestos plate on a stove and then heated inside of an iron crucible, having the bottom red hot. The caps of the Gooch crucibles were put on and the precipitates moistened with a few drops of concentrated nitric acid and ignited, being careful

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[1] This Journal, **25**, 907 (1903).

to keep the bottom of the platinum crucible not above a dull red heat. The precipitates were again moistened and heated. This was continued until the color of the precipitates was a very light yellow. The crucibles were then allowed to cool in a desiccator and weighed. The weight of bismuth was then calculated, the factor being 0.40058. Results by washing with ammonium sulphate:

Bismuth solution taken. cc.	Weight of precipitate found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
10	0.2020	0.0809	0.08037
20	0.4010	0.1606	0.16074
20	0.4033	0.1616	0.16074
25	0.4988	0.1998	0.20092
30	0.6102	0.2443	0.24111

Results by washing with ammonium nitrate.

Bismuth solution taken. cc.	Weight of precipitate found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
20	0.3935	0.1576	0.16074
20	0.3967	0.1589	0.16074
25	0.4896	0.1961	0.20092
25	0.4992	0.2000	0.20092
30	0.5988	0.2399	0.24111
30	0.5998	0.2403	0.24111

The first and third in the second series were slightly too acid, giving incomplete precipitation and low results.

Different amounts of the bismuth solution were then precipitated by the method of Miller and Frank.[1] The precipitates were filtered on a platinum Gooch crucible and treated as before.

Results by washing with ammonium sulphate:

Bismuth solution taken. cc.	Weight of precipitate found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
10	0.2003	0.0802	0.08037
10	0.2025	0.0811	0.08037
15	0.3028	0.1213	0.12056
20	0.4057	0.1625	0.16074
20	0.4034	0.1616	0.16074

The first precipitate, after the final weighing, was heated for twelve minutes with a good full flame of a Bunsen burner and lost 0.0038 gram; then with the same flame for thirty-eight minutes and lost 0.0029 gram; then for one hour and twenty-five minutes, losing 0.0031 gram; and when heated with a blast lamp

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[1] This Journal, **25**, 926 (1903).

for five minutes the loss was 0.0050 gram, showing that the igniting of the precipitate must be done very carefully.

Results by washing with ammonium nitrate:

Bismuth solution taken.	Weight of precipitate found.	Weight of bismuth found.	Weight of bismuth taken.
5	0.0994	0.0398	0.04018
10	0.2013	0.0806	0.08037
15	0.3011	0.1206	0.12056
20	0.3992	0.1599	0.16074
25	0.4985	0.1997	0.20092
30	0.6024	0.2413	0.24111
35	0.6995	0.2802	0.28129

From the above results we can see that the most accurate results are obtained by using the precipitation method of Miller and Frank,[1] washing with ammonium nitrate. These conditions, in detail, are as follows: To the bismuth nitrate solution ordinary acid ammonium molybdate is added in excess (four to five times the amount necessary for precipitation), no precipitate being formed at this point. Then a few drops of congo red are added, and very dilute ammonia from a burette, stirring all the time. The ammonia is added until the solution becomes pink, and then a drop or two of dilute nitric acid till the color is lilac. The bulk of the solution is then made up to 150 to 200 cc., and heated slowly on a stove, stirring once in a while. When the solution has reached a temperature between 50° and 60° C. it is filtered on a platinum Gooch crucible and washed with a 3 per cent. solution of ammonium nitrate until the bulk of the filtrate has reached from 400 to 500 cc. Then the crucible with its cap is placed in an air-bath and dried at 160° C. When thoroughly dry it is moistened with a few drops of concentrated nitric acid and heated at the tip of the flame of a Bunsen burner, being careful to prevent the bottom from becoming more than dull red. It is again moistened with concentrated nitric acid, ignited, and this continued until the precipitate is very light yellow in color, when its weight will become constant.

In order to compare this method with the volumetric method, different amounts of the bismuth nitrate solution were precipitated and the bismuth determined according to the method of Miller and Frank,[1] the same conditions being followed, and the solution being titrated according to their experiment, II.

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[1] This Journal, **25**, 926 (1903).

Bismuth solution taken. cc.	Potassium permanganate required. cc.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
15	26.95	0.1207	0.12056
15	26.9	0.1205	0.12056
20	35.7	0.1599	0.16074
20	36.15	0.1619	0.16074
25	45.35	0.2031	0.20092
25	45.25	0.2027	0.20092

This shows that the results obtained by the gravimetric method are as accurate as those found by the volumetric procedure.

CONCLUSIONS.

(1) To determine bismuth by the evaporation of a nitric acid solution of bismuth nitrate the operation must be conducted in porcelain, otherwise some bismuth trioxide is reduced.

(2) In the precipitation of ammonium bismuth molybdate the use of congo red is preferable to methyl orange, and in washing the precipitate ammonium nitrate is better than ammonium sulphate.

(3) Bismuth may be determined correctly by the ignition of bismuth ammonium molybdate to $Bi_2O_3.4MoO_3$ when the temperature of ignition is kept below a dull red heat.

QUANTITATIVE LABORATORY,
COLUMBIA UNIVERSITY,
December 3, 1904.

COLORIMETRIC DETERMINATION OF PHOSPHORUS.

BY THOMAS E. HEWITT.

Received November 26, 1904.

THE color given on passing hydrogen sulphide into an alkaline molybdate solution seemed favorable for a colorimetric determination of molybdenum, and indirectly of phosphorus. The following method has been developed on this basis:

Standard Molybdic Acid Solution.—One cc. = 0.004108 gram MoO_3, equivalent to 0.000073 gram phosphorus.

Standard Phosphomolybdate Solution.—One cc. = 0.000006+ gram of phosphorus, 5 cc. = 0.419 cc. of the standard molybdic acid solution; prepared by dissolving ammonium phosphomolybdate in about the theoretical amount of sodium hydroxide.

In the following experiments 12-ounce bottles, 2 inches square, were used. The standard solution was placed in the bottle filled