

filtered, and the precipitate washed, ignited and weighed. The weight of ferric oxide was 0.0026 gram, which is equivalent to 0.35 per cent. of metallic iron. The total percentage equalled 100.01. The time required for the complete analysis was two and a half hours.

## SEPARATION OF COPPER FROM ZINC.

The conditions which served for the separation of copper from nickel are applicable in its separation from zinc.

No. of exp.	CuSO <sub>4</sub> = Cu. Gram.	ZnSO <sub>4</sub> = Zn. Gram.	NH <sub>4</sub> NO <sub>3</sub> . Grams.	Conc. HNO <sub>3</sub> . cc.	Cur- rent. N.D <sub>100</sub> = A.	Time. Min- utes.	Deposited Cu. Gram.	Error. mg.
1	0.2457	0.25	3	0.25	5	9 15	0.2458	+0.1
2	0.2457	0.25	3	0.25	5	9 15	0.2460	+0.3

This is sufficient to show the possibilities of this method of analysis. At the present time other separations are in progress.

UNIVERSITY OF PENNSYLVANIA.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 84.]

## THE VOLUMETRIC DETERMINATION OF BISMUTH AS MOLYBDATE AND ITS SEPARATION FROM COPPER.<sup>1</sup>

BY HERMAN S. RIEDERER.

Received January 2, 1903.

AT THE present time the quantitative determination of bismuth is conducted in the great majority of cases by precipitation as bismuth basic carbonate by ammonium carbonate, in spite of the fact that many different schemes have been published for its separation from other metals and determination, using other reagents.

It was with the intention of finding, if possible, a reliable volumetric method equal in accuracy to the carbonate method, that this work was undertaken.

As the work progressed and the molybdate method was to be applied to ores, to show its practical value, it developed that a shorter and simpler separation of bismuth from copper, especially, would make the method complete from the ore, and it was then that the precipitation of bismuth with hydrogen sulphide from a solution containing tartaric acid and made alkaline with

<sup>1</sup> From author's thesis for the degree of Doctor of Philosophy. Read at the December meeting of New York Section of the American Chemical Society.

caustic potash and potassium cyanide was worked out and found satisfactory.

## EXPERIMENTAL.

For the experimental part of this work a bismuth nitrate solution was prepared and standardized by the following methods: (a) Direct evaporation to dryness of a measured volume and ignition of the dry nitrate to trioxide; (b) precipitation of basic carbonate, drying and igniting to trioxide. The results obtained by these two methods were further checked by precipitating the bismuth as sulphide, and carefully igniting this to the trioxide (c).

## (a) DIRECT EVAPORATION METHOD.

Bi(NO <sub>3</sub> ) <sub>3</sub> taken. cc.	Character of vessel used.	Found.	
		Bi <sub>2</sub> O <sub>3</sub> . Gram.	Bi. Gram.
5	porcelain.	0.0643	0.05765
5	“	0.0643	0.05765
6	“	0.0773	0.06931
20	platinum	0.2578	0.23084
30	“	0.3663	0.34636

## (b) CARBONATE METHOD.

Bi(NO <sub>3</sub> ) <sub>3</sub> taken. cc.	Found.	
	Bi <sub>2</sub> O <sub>3</sub> . Gram.	Bi. Gram.
20	0.2581	0.23140
20	0.2577	0.23106
20	0.2570	0.23042
25	0.3222	0.28888
30	0.3869	0.34689
10	0.1288	0.11548
11	0.1415	0.12687
12	0.1542	0.13826

## (c) SULPHIDE METHOD.

Bi(NO <sub>3</sub> ) <sub>3</sub> taken. cc.	Found.	
	Bi <sub>2</sub> O <sub>3</sub> . Gram.	Bi. Gram.
20	0.2575	0.23086
20	0.2578	0.23114

From these results the strength of the solution was taken to be 1 cc. = 0.01155 gram bismuth.

## ELECTROLYTIC METHODS.

It was deemed advisable to try some of the proposed methods

and that of Wimmenauer<sup>1</sup> looked promising. No satisfactory results could be obtained by it, however. Kammerer's<sup>2</sup> method was also tried with no better results, although Smith states in his book that it is probably the best of the proposed methods.

#### OXALATE METHODS.

Warwick and Kyle<sup>3</sup> proposed, apparently as a new method, the precipitation of bismuth as oxalate either with ammonium oxalate or oxalic acid, and heating to facilitate the reaction. The clear solution is then decanted, and the precipitate is boiled with successive portions of water to convert the precipitate to the basic oxalate. This is then dissolved in acid and the oxalic acid is titrated with standard potassium permanganate solution. Both ammonium oxalate and oxalic acid precipitate bismuth as oxalate, which, however, is easily soluble in excess of ammonium oxalate whether hot or cold. Owing to this fact, ammonium oxalate was not further tried in determining the value of the proposed method. Oxalic acid was then tried as described by Warwick and Kyle.

It was noted that this is nearly an exact copy of Muir's method.<sup>4</sup> The only great difference between them is that in Muir's method the precipitation is done in the cold, while Warwick and Kyle make their precipitation by heating, and also claim that two boilings with 50 cc. of water suffice to convert all the precipitate to the basic salt, while Muir says to boil with successive portions of water till the filtrates are free from acid. In the following experiments it was found that only very small amounts of oxalate could be converted by two boilings, while 0.0924 gram bismuth required three and four boilings with 80-100 cc. water to remove all free acid. The results in the following table were obtained by the factor calculated as given in the method by Warwick and Kyle. If 1 cc. of potassium permanganate equals 0.010 gram iron, it is equivalent to 0.0186 gram bismuth. One cc. of potassium permanganate used was equal to 0.005612 gram iron and hence equivalent to 0.01048 gram bismuth. This was the factor used. To show the irregularity of the results, the last column in the table shows what the factor for potassium permanganate to bismuth would be in each case according to the results obtained.

<sup>1</sup> *Ztschr. anorg. Chem.*, **27**, 1 (1901).

<sup>2</sup> "Electrochemical Analysis," Smith, 3rd edition (1902), p. 67; *This Journal*, **25**, 83 (1903).

<sup>3</sup> *Eng. and Min. J.*, April, 1901.

<sup>4</sup> *J. Chem. Soc. (London)*, **33**, 70 (1878).

## RESULTS.

Bi(NO <sub>3</sub> ) <sub>3</sub> taken. cc.	Bi taken. Gram.	KMnO <sub>4</sub> used. cc.	Bi found. Gram.	Calculated factors.
4	0.0451	3.8	0.0398	0.01186
6	0.0693	5.6	0.0587	0.01237
8	0.0924	8.4	0.0878	0.01100
10	0.1155	9.6	0.1006	0.01203
12	0.1386	12.4	0.1300	0.01117

These results being irregularly low, the cause was sought in the solubility of the oxalate. It was then found that the bismuth oxalate is slightly soluble in a hot solution containing oxalic acid. Apparently this fact was known to Muir, as in his method the bismuth is precipitated in the cold and the supernatant liquid is decanted. Then the precipitate, free from oxalic acid solution, is converted to the basic oxalate by boiling with water. The method was tried to ascertain its exactness so that it might be used for further standardization, if necessary. The results, however, were irregularly high, due to the difficulty experienced in converting to the basic salt. The precipitate is very fine and heavy and caused violent bumping. Four or more boilings were always necessary to free the washings from oxalic acid. The conversion had not even then been completed.

## RESULTS.

Bi(NO <sub>3</sub> ) <sub>3</sub> taken. cc.	Bi taken. Gram.	KMnO <sub>4</sub> used. cc.	Bi found. Gram.
4	0.0462	4.6	0.0482
6	0.0693	7.25	0.0775
8	0.0924	10.3	0.1079
10	0.1155	11.7	0.1226
12	0.1386	14.8	0.1551
14	0.1619	16.7	0.1750
8.1	0.0936	9.7	0.1016
9.9	0.1143	11.95	0.1252
4	0.0462	4.35	0.0456
6	0.0693	7.3	0.0765
14	0.1619	16.75	0.1755

In the last three determinations the precipitates were boiled several times after the conversion seemed to be complete, but the amount of oxalic acid retained was still higher than that calculated for the basic oxalate. The method did not seem practical for further work, as three other determinations started with these last three were lost by the violent bumping already mentioned.

Warwick and Kyle also claim that this method is a separation of bismuth from copper, arsenic, antimony and several other

metals. Copper being the most important, its behavior with ammonium oxalate and also oxalic acid was tried and it was found to act like bismuth in both cases, namely, it is soluble in excess of ammonium oxalate and insoluble in oxalic acid. After obtaining these results, it was not thought necessary to test the method of Warwick and Kyle further; as the principle of the method is old, the proposed changes render the method inaccurate, and the separations claimed are impossible.

These conclusions are further confirmed by Grabill,<sup>1</sup> who made a study of the reaction of bismuth with ammonium oxalate. He contradicts Warwick and Kyle, and also states that copper oxalate is insoluble.

Another proof that the separation of bismuth and copper is impossible by oxalic acid is given by the fact that Peters<sup>2</sup> precipitates copper quantitatively with this reagent and determines copper in this way.

#### THE MOLYBDATE METHOD.

When a solution of ammonium molybdate in nitric acid is added to a nitric acid solution of bismuth nitrate and the whole is neutralized with ammonia but not made alkaline, all the bismuth is precipitated as a molybdate in a fine flocculent form. If this is then warmed without boiling, the whole precipitate will collect into large, heavy flocks which settle very rapidly. This precipitate is easily washed by decantation and filters very rapidly. By the following work it was found that the molybdenum ratio to that of bismuth remains constant.

The limits of the precipitation are very narrow. The ammonium molybdate must be in large excess, three to four times the theoretical amount necessary for combining with all the bismuth. The original solution will contain about 5 per cent. of nitric acid, but this must be almost entirely neutralized with ammonia. To obtain this point, methyl orange is used as an indicator to get the solution neutral, and it is then acidified with 1 or 2 drops of 30 per cent. nitric acid. The whole is then heated on a thick asbestos pad over a small flame until the fine flocks have collected; generally the whole precipitate will rise from the bottom in large masses by the action of the hot circulating solution. The precipitate is then stirred to break it up, after which it is

<sup>1</sup> *Eng. and Min. J.*, 72, 354 (1901).

<sup>2</sup> *Ztschr. anorg. Chem.*, 26, 111 (1901).

allowed to settle. The precipitate is exceedingly heavy and settles in a few seconds, forming a compact mass. The supernatant liquid, which must be perfectly clear, is decanted through a plain filter-paper. Then the precipitate is washed twice by decantation with a 3 per cent. solution of ammonium sulphate, after which it is washed on the filter with the ammonium sulphate solution. It is then dissolved in dilute sulphuric acid and run through a Jones reductor with suction; after this, it is strongly acidified with sulphuric acid and is immediately titrated with standard potassium permanganate.<sup>1</sup>

The precipitation and washing were done in a small beaker and the bulk was about 200 cc. It was found best to heat slowly, as with fast heating the solution was liable to come to a boil, which makes the determination unreliable. A 3 per cent. solution of ammonium sulphate was found satisfactory for washing and was preferred to any other salt as it has only constituents of the solution which is run through the reductor, and as ammonium sulphate is inactive to zinc in acid solution and also to potassium permanganate. A reductor with a column of zinc 40 to 45 cm. in length in a tube 1.25 cm. in diameter was used, to avoid the necessity of more than one passage through the zinc, and the suction flask was so large that the titration was made in it directly. Thus air had less chance of reoxidizing the molybdous oxide, which was to be determined by permanganate.

The color of the molybdate precipitate is pure white. Sometimes, when the conditions were not followed exactly, a slightly yellowish to canary-yellow compound resulted which gave varying results, but always lower than the white compound. This yellow molybdate, when formed, could however easily be changed to the white, by first making the solution alkaline with ammonia to throw down bismuth oxyhydrate, and then dissolving this in nitric acid, all this being done in the whole mixture of precipitate and solution. The clear solution is now re-treated as a new solution except that it is not always necessary to add more ammonium molybdate.

The results given in the following tables are calculated for the value in bismuth of 1 cc. of the potassium permanganate solution. To compare the results obtained in this way with an absolute standard, several samples of the purest obtainable bismuth were

<sup>1</sup> For further details of precipitation see the following paper.

weighed out and treated like the standard  $\text{Bi}(\text{NO}_3)_3$  solution with very satisfactory results.

## RESULTS.

$\text{Bi}(\text{NO}_3)_3$ taken. cc.	Bi taken. Gram.	$\text{KMnO}_4$ used. cc.	Equivalent amount of bismuth of 1 cc. $\text{KMnO}_4$ .
9	0.10395	28.5	0.003647
9	0.10395	28.7	0.003621
15	0.17325	47.75	0.00328
16	0.18480	50.9	0.003630
8.5	0.09818	27.	0.003636
12.3	0.14207	30.8	0.004610 <sup>1</sup>
7.8	0.09009	24.8	0.003632
9.8	0.11319	31.15	0.003633
11.6	0.13398	30.	0.004466 <sup>1</sup>

The results with the yellow precipitates indicate a totally different compound containing more bismuth than the white precipitate.

The following results were obtained with metallic bismuth:

Bismuth taken. Gram.	$\text{KMnO}_4$ used. cc.	Value of 1 cc.
0.1100	30.1	0.003654
0.1398	38.3	0.003626
0.1084	29.8	0.003637
0.1434	39.5	0.003630
0.1815	50.0	0.003630

From these results, the value of the potassium permanganate solution was taken as 1 cc. = 0.003630 gram of bismuth.

If the degree of reduction<sup>2</sup> of the molybdenum obtained in a Jones reductor is assumed to correspond to  $\text{Mo}_{24}\text{O}_{37}$ , the ratio of bismuth to molybdenum in the white precipitate is 1 : 1.977, while in the yellow precipitates it approaches 1 : 1.5, the ratio for the well-known normal bismuth molybdate.

The ratio was determined gravimetrically as follows: 10 cc. of the bismuth nitrate solution were precipitated as molybdate under the usual conditions. This was decomposed with ammonium sulphide, which precipitated bismuth sulphide and held the molybdenum sulphide in solution. The bismuth sulphide was dissolved with hot, dilute nitric acid, and the bismuth determined by the evaporation method (a) as a check on the completeness of precipitation by ammonium molybdate. The molybdenum solution was acidified, saturated with hydrogen sulphide and heated in boiling

<sup>1</sup> Yellow precipitates.

<sup>2</sup> The degree of reduction of the molybdenum and the ratio of bismuth to molybdenum in this precipitate are discussed in the following paper.

water in a pressure bottle. The sulphide was filtered in a weighed platinum, Gooch crucible, washed with dilute sulphuric acid and with alcohol, then ignited very carefully and the oxide  $\text{MoO}_3$  weighed. The results were:

	A. Gram.	B. Gram.	C. Gram.
$\text{Bi}_2\text{O}_3$ found .....	0.1289	0.1285	0.1292
$\text{MoO}_3$ found .....	0.1058	0.1058	0.1057
Atomic ratios, Bi to Mo .....	1 : 1.985	1 : 1.99	1 : 1.982

These results were obtained on white precipitates; a yellowish precipitate analyzed in the same way gave a ratio of 1 : 1.71.

The ratio of bismuth and molybdenum in the compound having been found to be very nearly 1 : 2, it was evident that some other element or compound entered into the composition of the precipitate. It also showed that this molybdate was unknown in the literature, as the only molybdate of bismuth that could be found was the normal molybdate, ratio 2 : 3, a yellow compound soluble in 500 parts of water.<sup>1</sup> It was naturally supposed that ammonium was the missing factor in the compound, as no other base was employed. Attempts were made to obtain the molybdate pure and free from ammonium sulphate, so that the ammonia in combination could be determined. This was not found possible, as both water and 50 per cent. alcohol decomposed the compound, and no other available liquid could be found with which the ammonium sulphate could be washed out, leaving the pure molybdate behind. This peculiarity of the compound made it necessary to make an indirect determination for ammonia, by finding the total in the compound and combined as sulphate; then determining the sulphuric acid present and calculating its equivalent of ammonia; this subtracted from the total ammonia would give the ammonia in combination. A definite amount of bismuth was employed every time to avoid the necessity of determining this and the molybdenum in each portion.

The results did not check well, but showed conclusively that the precipitate contained ammonia, to the extent of about 1 molecule. Although these results are not sufficiently accurate to prove the formula, they show that the compound is a new bismuth ammonium molybdate with a ratio of bismuth to molybdenum very close to 1 : 2. The formula  $\text{BiNH}_4 (\text{MoO}_4)_2$  would satisfy these facts.

It should be emphasized here that the precipitate is pure white;

<sup>1</sup> Storer's "Dictionary of Solubilities."



that if it is yellow it is undoubtedly contaminated by the normal molybdate, and that it is formed when the clear nitric acid solution containing an excess of molybdate is slowly neutralized with dilute ammonia, and then warmed but not boiled. As the conditions for this precipitation are narrow, and the degree of the reduction of molybdenum variable,<sup>1</sup> it is evident that care and strictly uniform conditions are essential to the success of the method.

#### THE SEPARATION OF BISMUTH AND COPPER.

The exactness of the molybdate method for bismuth having been proved, it was thought advisable to find a shorter separation from copper, so as to make the method of practical value, if possible. The ammonium carbonate method is a perfect separation, if it is repeated several times, in presence of large amounts of copper. Naturally this method is slow.

Pretzfeld,<sup>2</sup> in his new separation of mercury from copper, arsenic, and antimony by hydrogen sulphide in a potassium cyanide solution containing tartaric acid, found that, among a few other metals, bismuth also interferes; he did not, however, determine whether it was completely precipitated. A few experiments showed that all the bismuth was thrown out of solution by Pretzfeld's conditions; namely, the acid solution is neutralized with potassium cyanide after about 30 cc. of a saturated tartaric acid solution have been added; enough potassium cyanide must be added to dissolve any precipitate which may form, except bismuth sulphide thrown out by the sulphur in the cyanide. This alkaline solution is now saturated with hydrogen sulphide gas, and the bismuth sulphide is filtered out. The filtrate is colorless to light lemon-yellow. When copper was added to the bismuth solution and the above conditions were applied, the deep red color mentioned by Pretzfeld was present every time, in spite of the presence of tartaric acid.

When the bismuth copper mixture was first made alkaline with caustic potash, after adding tartaric acid, and potassium cyanide was added till the solution was clear, neither a red color appeared, nor was it necessary to use more than a small amount of potassium cyanide. The solution, even after saturation with hydrogen sulphide was never darker than a light lemon-yellow. The most important points were, however, that all the bismuth was precipi-

<sup>1</sup> See following article.

<sup>2</sup> Dissertation, "The Determination and Separation of Mercury," Columbia University, 1902. This Journal, 28, 205 (1903).

tated as sulphide in small bulk, all copper remained in solution and the filter-paper could be washed free from copper with potassium cyanide solution or pure water, and pure bismuth sulphide remained.

## RESULTS.

Bi(NO <sub>3</sub> ) <sub>3</sub> taken. cc.	Bi taken. Gram.	Cu. Gram.	Bi <sub>2</sub> O <sub>3</sub> found. Gram.	Bi found. Gram.
10	0.1155	0.5	0.1285	0.11521
10	0.1155	0.5	0.1287	0.11539
10	0.1155	1.0	0.1284	0.11512

The bismuth sulphide was dissolved in nitric acid, and then the bismuth was reprecipitated as basic carbonate which was ignited to oxide and weighed.

## ANALYSIS OF BISMUTH ORES.

Two samples of bismuth ores containing iron, but free from copper, were obtained and these were used to show the exactness of the new method, as compared to the basic carbonate method.

From 0.3 gram to 0.5 gram of the richer ore were used for analysis and treated as follows: The ore was decomposed with nitric acid and was evaporated with sulphuric acid to fumes; after dilution, the residue was filtered off and re-treated with nitric and sulphuric acids as before. The filtrates were combined and diluted to about 750 cc. Then bismuth sulphide was precipitated with hydrogen sulphide and filtered out. For the carbonate method, this sulphide was dissolved in hot dilute nitric acid and precipitated by adding ammonia and ammonium carbonate, and heating. The precipitated basic carbonate was filtered, washed and ignited in a weighed porcelain crucible. To insure against any reduction of metal by the burning of the paper, the carbonate was dissolved through the paper, into the crucible, with hot dilute nitric acid.

For the molybdate method, the bismuth sulphide was also dissolved in nitric acid and this solution was treated with tartaric acid, potassium hydroxide, potassium cyanide and hydrogen sulphide, to free the bismuth of impurities which would interfere in the molybdate method. The pure bismuth sulphide was again dissolved in nitric acid, precipitated as molybdate, dissolved, reduced, and titrated. The following results show the comparative accuracy of the two methods.

## RESULTS.

Ore taken. Gram.	Bi <sub>2</sub> O <sub>3</sub> . Gram.	Bi found. Gram.	Per cent.
0.5001	0.1096	0.0983	19.65
0.5004	0.1098	0.0984	19.67
0.5008	0.1098	0.0984	19.65
0.5009	0.1095	0.0982	19.60
Ore taken. Gram.	KMnO <sub>4</sub> used. <sup>1</sup> cc.	Bi found. Gram.	Per cent.
0.5000	29.6	0.0987	19.74
0.3011	17.8	0.0594	19.71
0.3003	17.6	0.0589	19.61

The second ore was similar to the first. The same scheme of analysis was employed.

## RESULTS.

Ore taken. Gram.	Bi <sub>2</sub> O <sub>3</sub> . Gram.	Bi found. Gram.	Per cent.
1.0002	0.0843	0.0756	7.55
0.7506	0.0620	0.0556	7.41
Ore taken. Gram.	KMnO <sub>4</sub> used. <sup>1</sup> cc.	Bi found. Gram.	Per cent.
0.7505	17.0	0.0567	7.55
0.5008	11.4	0.0380	7.57

## ANALYSIS OF COPPER MATTE CONTAINING BISMUTH.

At the time these analyses were under way, no matte containing bismuth was on hand, so a convenient amount of bismuthinite was mixed and ground up with a matte to make it about 0.5 per cent. to 0.6 per cent. bismuth. This was then analyzed by the two methods, as with the ores.

The method of procedure was similar to that employed in the ores, except that decomposition was effected with nitric and hydrochloric acids, no sulphuric acid being used. For the basic carbonate method the bismuth was precipitated alternately with hydrogen sulphide in acid solution and then with ammonium carbonate in ammoniacal solution to free the bismuth of iron and copper. Otherwise the methods were the same. It may be noted that only one precipitation was necessary for bismuth with hydrogen sulphide in the tartaric acid, potassium hydroxide, and potassium cyanide solution to obtain the bismuth free from copper. For one determination by the molybdate method, the standard permanganate solution was diluted to one-tenth the strength to reduce the error in titration, as the amount of bismuth was so small.

<sup>1</sup> Factor : 1 cc. KMnO<sub>4</sub> = 0.003335 gram Bi.

## RESULTS.

Matte taken. Gram.	Bi <sub>2</sub> O <sub>3</sub> found. Gram.	KMnO <sub>4</sub> used. cc.	Per cent.
2.2433	0.0134	...	0.597
2.5295	0.0164	...	0.648
2.0004	0.0126	...	0.565
2.2294	.....	3.9	0.583
2.0032	.....	3.25	0.541
2.0935	.....	3.4	0.542
2.0020	.....	34.2 $\frac{\text{standard}}{10}$	0.553

The molybdate method was applied to the matte in the most unsatisfactory way, as only small samples were used. When, however, enough sample is on hand, in case of a matte low in bismuth, it is advisable to take 5 grams to 10 grams or more to start with, as no difficulty will be experienced in separating the copper, and the quantity of bismuth will be enough for convenient handling by the molybdate method. Small amounts of bismuth are more difficult to precipitate as molybdate, and the titration is not as reliable when only a few cubic centimeters of potassium permanganate are employed.

## CONCLUSIONS.

The method proposed by Warwick and Kyle is founded on an old principle and the changes made by them make it worthless.

Bismuth is completely precipitated by hydrogen sulphide from a solution treated as follows: Tartaric acid is added to the acid solution; it is then made alkaline with caustic potash, a slight excess of potassium cyanide is added and the solution is precipitated with hydrogen sulphide. Under these conditions copper will remain in the solution. Small amounts of bismuth are quickly and easily separated from large amounts of copper in this way.

Bismuth is completely precipitated as bismuth ammonium molybdate by ammonium molybdate in a solution just acid with nitric acid. This precipitate can be washed with a 3 per cent. ammonium sulphate solution, and used for the determination of bismuth by dissolving in sulphuric acid, reducing the molybdenum and reoxidizing with potassium permanganate as in the method for phosphorus.

This separation and determination give a method equal in accuracy to the basic carbonate method, while the time necessary, especially when large amounts of copper are present, is very much less.

This work was carried out under the direction of Professor Edmund H. Miller, and it is with great pleasure that I take this opportunity of thanking him for the counsel and kind encouragement which he extended to me throughout the research.

QUANTITATIVE CHEMICAL LABORATORY,  
HAVEMEYER HALL, COLUMBIA UNIVERSITY,  
November 1, 1902.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 85.]

## ON THE REDUCTION OF MOLYBDENUM BY ZINC AND THE RATIO OF BISMUTH TO MOLYBDENUM IN BISMUTH AMMONIUM MOLYBDATE.

BY EDMUND H. MILLER AND HENRY FRANK.

Received June 24, 1903.

NUMEROUS investigations have been made on the reduction of molybdenum by zinc in a reductor. W. A. Noyes<sup>1</sup> and Frohman came to the conclusion that the reduction corresponded to a salt of the oxide  $\text{Mo}_2\text{O}_3$ , provided that the air is displaced by carbon dioxide in the titrating flask. Blair<sup>2</sup> and Whitfield, however, although they followed Noyes and Frohman's conditions, could never attain a reduction equivalent to the oxide  $\text{Mo}_2\text{O}_3$ , but almost invariably obtained reduction equivalent to an oxide,  $\text{Mo}_{24}\text{O}_{37}$ . Other investigators have either confirmed the results of Blair and Whitfield or come to the conclusion that the reduction did not proceed even as far as  $\text{Mo}_{24}\text{O}_{37}$ , but to a point corresponding to an oxide of the formula  $\text{Mo}_{12}\text{O}_{19}$ . Drown,<sup>3</sup> however, by the use of 100-mesh zinc in a closed flask, has obtained a reduction corresponding to the oxide  $\text{Mo}_2\text{O}_3$ .

It was the object of this work to study the extent of the reduction produced in a reductor when the conditions, such as the length of the column of zinc, the acidity, the temperature and the atmosphere were varied, and to see whether the oxide  $\text{Mo}_2\text{O}_3$  could be reached (Part I). And also, when the conditions for a definite degree of reduction were obtained, to apply these to the confirmation of the ratio of bismuth to molybdenum in the new bismuth

<sup>1</sup> This Journal, 16, 553.

<sup>2</sup> *Ibid.*, 17, 747.

<sup>3</sup> Blair's "Chemical Analysis of Iron," 4th edition, p. 99.