ON THE ANALYSIS OF BISMUTH BY MEANS OF SELENIOUS ACID.

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Berg and Teitelbaum[1] measured the sensitivity of formation of bismuth selenite precipitate in 1/3 and 1/4 normal nitric acid, and they fixed the limit of detectability of bismuth at 0.000016 g. in 5 ml., i.e. 1:300000. They state that an accurate gravimetric analysis can be made by making the precipitate, having the composition $Bi_2(SeO_3)_3 \cdot H_2O$, anhydrous by boiling in the mother liquor and then by properly drying and weighing.

For satisfactorily accomplishing the analysis of bismuth by the use of selenious acid as the precipitant, it is important to have a clear knowledge of the relation of the acid concentration to the formation of the precipitate, and of the behaviour of other metals upon selenious acid. The present investigation was started for clarifying these points.

The Material and Reagents. The material for the experiments was prepared from the selenium of the Hitachi Mine by heating it in the stream of oxygen, purifying the selenium oxide by repeated resublimation, adding a

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small quantity of freshly boiled water, and evaporating on the water-bath. For oxidizing any liberated selenium, the evaporation was continued with the addition of 3–4 ml. of concentrated nitric acid, and the residue was finally heated over direct flame until white fumes were developed. The selenious acid thus prepared was used as a 5 per cent. aqueous solution.

Kahlbaum's bismuth nitrate of the superior quality and Merck's nitric acid of sp. gr. 1.4 for analytical use were employed for making 1% solution of the former and 0.5 N solution of the latter.

The Sharpness of the Reaction leading to the Formation of Bismuth Selenite Precipitate. For the purpose of ascertaining the limits of formation of bismuth selenite precipitate, observations were made under the conditions of reaction detailed in Table 1.

Table 1.

Bi taken (g.)	Selenious acid solution (ml.)	Total volume (ml.)	Nitric acid normality	Limit of formation of ppt.	Remarks
0.000043	1.3	4.3	1/3.3	1×10^{-5}	Immediate white turbidity; crystalline particles on heating. Clear supernatant liquid.
,,	1.6	8.6	1/4.3	2×10^{-5}	Fine cryst. particles on heating 1 minute.
,,	1.9	12.9	1/3.9	3×10^{-5}	Fine cryst. particles on heating 2 minutes.
,,	2.05	15.05	1/3.8	3.5×10^{-5}	Fine cryst. particles on heating 2 minutes.
,,	2.0	17.2	1/3.7	4.0×10^{-5}	A few fine cryst. particles on heating 2 minutes.
,,	2.5	21.5	1/3.6	5.0×10^{-5}	A few fine cryst. particles on heating 2-3 minutes. Clearly distinct from the blank test.
0.000086	1.5	4.5	1/3.4	5.0×10^{-5}	The same as above.

From the above-given results, it is seen that 0.00001 g. of Bi in 5 ml. can be detected when the final acid normality is 1/4. The sensitiveness is 1:500000.

The Influence of Acid Strength on the Sensitivity of Precipitation. If the acidity is above 0.86 N in nitric acid, the precipitation of bismuth selenite is incomplete even when 0.00086 g. of Bi is contained in 6 ml. of the solution. Beyond 1 N in acidity, there is no precipitation at all. It is found that, for the complete precipitation, the acidity must be below 0.5 N. The influence of hydrochloric acid is about the same as that of nitric acid. Sulphuric acid is, however, very much weaker in this respect, for up to 1.4 N it does not hinder the precipitation of a solution of 0.00086 g. Bi in 5–6 ml., while nitric acid completely prevents the precipitation already at 0.9 N. When heated, nitric acid prevents the precipitation at 0.6 N while with sulphuric acid the limit is reached only at 0.9 N.

The Action of Selenious Acid upon the Salts of other Metals. Such metals as Cu, Cd, $Fe^{\cdot\cdot}$, Al, Ni, Co, Mn, Zn, Ca, Li, Na, and K are not precipitated by selenious acid and can be separated from bismuth by its use. Iron and chromium in the trivalent state are precipitated within 15 minutes by heating at the concentration of 4.5×10^{-5} and 5×10^{-4} respectively. The iron precipitate is dissolved by 1/6 N HNO_2, 2/7 N HCl, and 1/3 N H_2SO_4. The chromium precipitate is dissolved by 1.7 N HNO_3, 0.7 N HCl, and 1.2 N H_2SO_4.

Solution of such metals as Hg, Pb, $Sn^{\cdot\cdot}$, Sb, and Ag are precipitated by selenious acid at the concentration of 7.5×10^{-4} to 1.5×10^{-5}. The lead precipitate is readily soluble in HNO_3 or HCl. Solutions of Ba, Sr, Mg, Ti, and Th are precipitated at the concentration of 5×10^{-4} to 2×10^{-5}, and the precipitates of Ba, Sr, and Th are dissolved in the presence of 1.1–2 N HCl, or 0.7–1.2 N HNO_3. Among the twelve elements mentioned above which are precipitable with selenious acid, silver, ferric iron, barium, titanium, and thorium are more sensitive than the rest, and consequently their presence makes the qualitative detection of bismuth somewhat uncertain. As bismuth, mercury, and lead have the common properties of being precipitated by H_2S and of not dissolving in ammonium sulphides, their detection will have nothing to gain by the use of selenious acid reagent.

The Quantitative Determination of Bismuth with Selenious Acid. Fifty ml. of 1% solution of bismuth nitrate are diluted to 80–90 ml. and nitric acid is added to the resultant strength of 0.35–0.38 N. The solution is heated to boiling and the selenious acid reagent is added slowly with stirring. After the completion of precipitation, an excess of a few ml. of the reagent is added while still keeping the solution boiling for some time. After cooling the precipitate is filtered and washed with cold water until there is no selenious acid remaining in the filtrate. The precipitate is well dried in the air and is then ignited rather strongly from the outset over the Bunsen burner for an hour (If the heating is begun slowly with a small flame, there is

a danger of a loss of bismuth in the stream of subliming SeO_2 formed by the decomposition of the precipitate). After cooling it is weighed in the usual manner.

It is to be noted here that if the heating is done, as suggested by Berg and Teitelbaum, at first for an hour at 50° and for another hour at 105°–115°, and the precipitate is weighed as $Bi_2(SeO_3)_3$, it is rather difficult to attain a constant result (Table 2).

Table 2.

Product finally weighed	Theoretical value (g.)	Values found (g.)		
		1	2	3
$Bi_2(SeO_3)_3$	0.4031	0.3948	0.4029	0.3979
Bi_2O_3	0.2349	0.2348	0.2349	0.2347

It is seen from the Table that a more accurate and constant result is obtained by strongly igniting the bismuth selenite precipitate and weighing the product as Bi_2O_3, than by drying is at 105°–115° and weighing as $Bi_2(SeO_3)_3$.

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