Estimation of Elements as Selenides

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Abstract

1. The method of forming seleno salts and then decomposing them with excess of acid for the precipitation of selenides was extended to the estimation of molybdenum, iridium and indium.

2. It was found possible to estimate cadmium, bismuth, lead and zinc as selenides by direct precipitation with sodium selenide reagent.

3. It was found that copper, nickel, cobalt and manganese cannot be estimated as selenides for various reasons.

In an earlier publication[1]) the authors dealt with the quantitative estimation of arsenic, antimony, tin, rhenium, mercury, platinum, palladium, ruthenium, rhodium and gold as selenides and showed that these elements could be estimated by first forming the seleno salt and then decomposing it with acid. This method was extended for the estimation of iridium, indium and molybdenum and very satisfactory results were obtained.

The ease and accuracy with which these elements can be estimated as selenides by decomposing the seleno salts showed that it may be possible to apply this method also to the estimation of those metals which do not form seleno salts but are precipitated completely as selenides from acid or alkaline solutions. A study of the behaviour of metals, like bismuth, cadmium, lead and zinc, with sodium selenide has shown that under proper conditions these metals can be precipitated and estimated as selenides with remarkable ease and accuracy. This method is particularly useful and expeditious in the case of cadmium and bismuth. All the estimations were carried out in the special apparatus devised for preventing the oxidation of sodium selenide and contamination of the atmosphere with hydrogen selenide.

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[1]) I. K. Taimni and R. Rakshpal, Anal. Chim. Acta 25, 438 (1961).

Determination of Elements as Selenides

1. Materials

The most important of these is the alkali selenide solution which is required for precipitating the element as selenide. This is prepared from sodium hydroxide according to the method described earlier[1]).

The other materials used in the various estimations were of B. D. H. (Anala R quality) or Kahlbaum's. The solutions prepared from these materials were carefully standardized by well-known methods.

All experiments were carried out as indicated in the general method for the estimation of selenides in the previous paper[1]) from this laboratory.

2. Molybdenum

Apart from volumetric methods there are a number of gravimetric methods for the estimation of molybdenum, those based on lead acetate[2]), 8-hydroxyquinoline[3]) and sodium sulphide[4]) being well-known. The method of estimating molybdenum as selenide, based on the decomposition of the seleno salt is not only simple but gives quite satisfactory results.

For the estimation of molybdenum as selenide a pure sample of ammonium molybdate was dissolved in water and the amount of molybdenum in the solution was determined by precipitating it with 8-hydroxyquinoline[3]). Measured volumes of the molybdate solution were treated with an excess of freshly prepared 2 N sodium selenide reagent, the solution containing the seleno salt was treated with an excess of concentrated hydrochloric acid to produce an acidity of 4 N in the resulting solution, the black precipitate of the selenide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with water, alcohol and ether successively, sucked dry at the filter pump for five minutes, dried in a vacuum desiccator for half an hour and weighed. The weight of the precipitate corresponded with the formula $MoSe_3$.

The weights of molybdenum contained in a measured portions of the solution and those corresponding with the precipitates actually obtained are given in Table I.

3. Iridium

Iridium is usually estimated gravimetrically by the method which depends upon its precipitation as sulphide from a hot solution containing 20% hydrochloric acid by volume. The precipitate is strongly ignited, cooled in a

[2]) H. B. Weiser, J. Phys. Chem. **20**, 640 (1915).
[3]) W. Hartmann, Z. anal. Chem. **83**, 470 (1931).
[4]) I. K. Taimni and R. P. Agarwal, Anal. Chim. Acta **9**, 203 (1953).

Table I

Determination of Molybdenum with 2N Sodium Selenide reagent

No.	Vol. of Mo soln. in ml	Vol. of rea-gent added in ml	Vol. of 12N HCl added in ml	Wt. of ppt. MoSe$_3$ in g	Wt. of Mo in the ppt. in g	Wt. of Mo actually pre-sent in g
1	25	50	50	0.2511	0.07241	
	25	55	55	0.2511	0.07241	0.07273
	25	50	50	0.2511	0.07241	
2	20	50	50	0.2008	0.05789	
	20	45	45	0.2009	0.05792	0.05818
	20	50	50	0.2008	0.05789	
3	10	20	20	0.1004	0.02895	
	10	25	25	0.1004	0.02895	0.02909
	10	20	20	0.1004	0.02895	

current of hydrogen and weighed as metal. It has been shown that it can also be estimated directly as sulphide by the sodium sulphide method[5]).

In the estimation of iridium as selenide, it was found that though the selenide is precipitated by decomposing the seleno salt with acetic acid and ammonium acetate as in the case of palladium, platinum, ruthenium and rhodium, the precipitate passes through the filter in colloidal form. Further investigations were made in order to find out whether it was possible to pre-cipitate iridium selenide in a form in which it could be filtered satisfactorily. It was found that if the seleno salt was decomposed with concentrated hy-drochloric acid in the presence of a small quantity of ammonium chloride, the selenide could not only be precipitated in an easily filtrable form, but was in such a condition that it could be weighed directly for the estimation of the element.

For estimating iridium as selenide a solution of iridium sodium chloride was prepared and standardized by the sulphide method referred to above. Measured volumes of the solution were treated with a large excess of freshly prepared 2 N sodium selenide reagent to form the seleno salt. This was then decomposed with concentrated hydrochloric acid. After stirring the mixture by passing carbon dioxide it was treated with a little ammonium chloride. The dark-brown precipitate of iridium selenide was filtered through a weighed sintered glass crucible (porosity 4) at a low pressure, washed thoroughly with water, alcohol and ether successively, sucked dry at the filter pump, dried for 30 minutes in a vacuum desiccator and weighed. The weight of the precipitate corresponded with the formula Ir$_2$Se$_3$.

[5]) I. K. TAIMNI and G. B. S. SALARIA, Anal. Chim. Acta 11, 329 (1954).

The weights of iridium contained in the measured portions of the solution and those corresponding with the precipitates actually obtained are given in Table II.

Table II
Determination of Iridium with 2N Sodium Selenide reagent

No.	Vol. of Iridium solution in ml	Vol. of Reagent added in ml	Vol. of 12N HCl added in ml	Wt. of ppt. Ir_2Se_3 in g	Wt. of Ir in the ppt. in g	Wt. of Ir actually present in g
1	10	20	20	0.0361	0.02238	
	10	20	20	0.0361	0.02238	0.02240
	10	18	18	0.0361	0.02238	
2	20	45	40	0.0720	0.04462	
	20	50	45	0.0720	0.04462	0.04480
	20	50	50	0.0721	0.04468	
3	25	50	50	0.0898	0.05565	
	25	55	50	0.0898	0.05565	0.05600
	25	55	50	0.0899	0.05572	

4. Indium

The behaviour of indium salts with sodium selenide has shown that indium can be estimated as selenide with great ease and accuracy. If the solution containing indium was treated with freshly prepared sodium selenide, at first, a precipitate was obtained which dissolved on adding excess of the reagent. The clear solution was then treated with excess of acetic acid and the precipitated selenide was weighed as In_2Se_3 after suitable treatment.

A solution of indium chloride was prepared by dissolving pure indium metal in dilute hydrochloric acid and standardized by precipitating the hydroxide and igniting the precipitate to In_2O_3. Measured volumes of this solution were treated with ammonium hydroxide solution to neutralize the hydrochloric acid until a slight turbidity appeared and then with an excess of freshly prepared 2 N sodium selenide reagent until the precipitate which was obtained in the first instant, dissolved giving a clear solution. The indium selenide was then precipitated by adding excess of acetic acid and shaking the mixture thoroughly. The orange voluminous precipitate of indium selenide was filtered throuhg a weighhed sintered glass crucible (porosity 4), washed thoroughly with hot water, alcohol and ether successively, sucked dry at the filter pump for five minutes, dried in a vacuum desiccator for about 30 minutes and weighed. The weight of the precipitate corresponded with the formula In_2Se_3. The colour of the precipitate changed to red on drying.

The weights of indium obtained in the measured portions of the solution and those corresponding with the precipitates actually obtained are given in Table III.

Table III

Determination of Indium with 2N Sodium Selenide reagent

No.	Vol. of Indium soln. in ml	Vol. of reagent added in ml	Vol. of 8N Acetic acid added in ml	Wt. of ppt. In_2Se_3 in g	Wt. of In in the ppt. in g	Wt. of In actually present in g
1	10	20	25	0.0375	0.01845	
	10	25	30	0.0376	0.01850	0.01854
	10	20	25	0.0375	0.01845	
2	20	45	50	0.0751	0.03696	
	20	45	50	0.0751	0.03696	0.03708
	20	50	55	0.0752	0.03701	
3	25	60	70	0.0940	0.04626	
	25	65	75	0.0940	0.04626	0.04635
	25	60	70	0.0940	0.04626	

In the case of the following four metals no seleno salt is found in solution but the metals can be precipitated directly as selenides by the addition of the sodium selenide reagent.

5. Cadmium

For estimating cadmium as selenide, a solution of cadmium sulphate was prepared and standardized by the sodium sulphide method[7]) or as $CdSO_4$[8]). Measured portions of the solution were treated with a large excess of freshly prepared 2 N sodium selenide reagent to precipitate the cadmium as selenide. In this case the precipitating reagent, has to be added in small portions at a time with constant shaking in order to obtain a granular precipitate, which is brick-red in colour. The whole mixture was shaken thoroughly and kept aside for five minutes before filtration. If the precipitating reagent is added all atonce, the results obtained under these conditions are too high. The precipitate of cadmium selenide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with cold water, alcohol and ether successively, sucked dry at the filter pump for five minutes only, dried in a vacuum desiccator for 30 minutes and weighed as CdSe. The whole estimation can be completed in about two hours.

6) THIEL and KOELSCH, Z. anorg. Chem. 66, 288 (1910).

7) I. K. TAIMNI and G. B. S. SALARIA, Anal. Chim. Acta 11, 54 (1954).

8) W. F. HILLEBRAND and G. E. F. LUNDELL, 'Applied Inorganic Analysis', published by John Wiley & Sons, New York 1929.

The weights of cadmium contained in the measured portions of the solution and those corresponding with the precipitates actually obtained are given in Table IV.

Table IV
Determination of Cadmium with 2N Sodium Selenide reagent

No.	Vol. of cadmium solution in ml	Vol. of the Reagent added in ml	Wt. of ppt. CdSe in g	Wt. of Cd in the ppt. in g	Wt. of Cd actually present in g
1	10	20	0.0824	0.04840	
	10	18	0.0824	0.04840	0.04853
	10	20	0.0823	0.04834	
2	20	40	0.1648	0.09681	
	20	45	0.1648	0.09681	0.09706
	20	40	0.1647	0.09674	
3	25	60	0.2060	0.12100	
	25	55	0.2061	0.12110	0.12132
	25	55	0.2060	0.12100	

6. Bismuth

For the estimation of bismuth as selenide a solution of bismuth chloride was prepared by dissolving bismuth carbonate in hydrochloric acid and standardized[9]) by precipitating the metal as carbonate and igniting to Bi_2O_3. A measured volume of this solution was treated with ammonium hydroxide till a slight turbidity began to appear in the solution. It was then treated with freshly prepared 2 N sodium selenide reagent, the mixture was shaken thoroughly and treated with equal volume of 2 N hydrochloric acid, the black precipitate of bismuth selenide was filtered through a weighed sintered glass crucible (porosity 4) at a low pressure, washed thoroughly with water, alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for about half an hour and weighed. (About 20 ml of the sodium selenide reagent was required for 50 mg of the element. If the precipitating reagent is used in large excess, the results tend to be low). The weight of the precipitate corresponds with the formula Bi_2Se_3.

The weights of bismuth contained in the measured portions of the solution and those corresponding with the precipitates actually obtained are given in Table V.

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⁹) P. JANASCH, Z. anorg. Chem. 8, 302 (1895).

Table V
Determination of Bismuth with 2N Sodium Selenide reagent

No.	Vol. of Bismuth solution in ml	Vol of reagent added in ml	Vol. of 2N HCl added in ml	Wt. of ppt. Bi_2Se_3 in g	Wt. of Bi in the ppt. in g	Wt. of Bi actually present in g
1	10	15	15	0.0676	0.04314	
	10	12	15	0.0676	0.04314	0.04300
	10	15	15	0.0675	0.04308	
2	20	25	25	0.1352	0.08630	
	20	25	25	0.1351	0.08622	0.08600
	20	25	25	0.1352	0.08630	
3	25	30	30	0.1690	0.10787	
	25	35	35	0.1690	0.10787	0.10750
	25	30	35	0.1689	0.10781	

7. Lead

A careful study of the conditions under which lead can be precipitated as selenide has shown that the method of precipitation of selenide by adding excess of alkali selenide is applicable to this element also provided the solution is treated with solid ammonium acetate after the treatment with sodium selenide. The precipitation of lead selenide is not complete unless ammonium acetate is added in large excess. The precipitate of lead selenide can be weighed directly as PbSe.

For estimating lead as selenide a solution of lead acetate was preparad with acetic acid and standardized by precipitating it as $PbMoO_4$[10]) or $PbCrO_4$[11]). Measured portions of this solution were treated with ammonium hydroxide till a slight turbidity appeared and then with excess of freshly prepared 2 N sodium selenide reagent. The mixture was shaken thoroughly and, after most of the lead had been precipitated, was treated with about 10—15 gram of solid ammonium acetate to complete the precipitation. The black precipitate of lead selenide was filtered, through a weighed sintered glass crucible (porosity 4) washed thoroughly with cold water containing 5% alcohol, alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for about half an hour and weighed. The weight of the precipitate corresponds with the formula PbSe.

The weights of lead contained in the measured portions of the solution and those corresponding with the precipitates actually obtained, are given in Table VI.

[10]) Smith and Brandbury, Ber. **24**, 2930 (1891).
[11]) Pellet, Bull. Soc. Chim. **26**, 248 (1876).

Table VI
Determination of Lead with 2N Sodium Selenide reagent

No.	Vol. of Lead solution in ml	Vol. of the reagent added in ml	Wt. of ppt. PbSe in g	Wt. of Pb in the ppt. in g	Wt. of Pb actually present in g
1	10	15	0.0694	0.05024	
	10	15	0.0694	0.05024	0.05008
	10	12	0.0693	0.05017	
2	20	30	0.1388	0.10050	
	20	35	0.1387	0.10043	0.10016
	20	35	0.1388	0.10050	
3	25	40	0.1736	0.12570	
	25	35	0.1736	0.12570	0.12520
	25	35	0.1735	0.12563	

8. Zinc

For estimating zinc as selenide a solution of zinc chloride was prepared by dissolving zinc oxide in hydrochloric acid and standardized by precipitating the metal as $ZnNH_4PO_4$[12] Measured portions of this solution were treated with sodium hydroxide solution until a slight turbidity appeared in the solution. The solution was then treated with an excess of freshly prepared 2 N sodium selenide reagent in small portions and with constant shaking. The zinc selenide precipitate was filtered through a weighed sintered glass cru-

Table VII
Determination of Zinc with 2N Sodium Selenide reagent

No.	Vol. of zinc solution in ml	Vol. of reagent added in ml	Wt. of ppt. ZnSe in g	Wt. of Zn in the ppt. in g	Wt. of Zn actually present in g
1	25	50	0.1335	0.06046	
	25	55	0.1334	0.06042	0.06010
	25	50	0.1335	0.06046	
2	20	40	0.1067	0.04832	
	20	45	0.1067	0.04832	0.04808
	20	40	0.1066	0.04827	
3	10	25	0.0533	0.02414	
	10	25	0.0533	0.02414	0.02404
	10	20	0.0532	0.02409	

[12] W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT and G. I. HOFFMANN, Applied Inorganic Analysis, John Wiley and Sons, New York 1953.

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cible (porosity 4) at a low pressure, washed thoroughly with water, alcohol and ether successively, sucked dry at the filter pump, dried in a vacuum desiccator for about half an hour and weighed. The weight of the precipitate corresponded with the formula ZnSe.

The weights of zinc contained in measured portions of the solution and those corresponding with the precipitates actually obtained are given in Table VII.

A note on the behaviour of Copper, Nickel, Cobalt and Manganese with the Sodium Selenide reagent

As is well known the estimation of these elements as sulphide has not been found possible because of various difficulties. In the case of nickel and cobalt, the precipitate tend to form colloidal solution and a portion of the metal thus passes into the filtrate and in the case of copper there is catalytic oxidation of the sulphide. Similarly, in the case of sodium selenide reagent it was found that these elements, referred to above as well as manganese, cannot be estimated as selenides. In the case of copper there is catalytic oxidation and in the case of nickel, cobalt and manganese there is the formation of the colloidal solution on treatment with excess of the sodium selenide reagent. So these elements could not be estimated as selenides and require further investigations.

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