APPLICATION OF SELENIUM SALTS IN INORGANIC ANALYSIS

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Several papers[1,2] have appeared from this laboratory dealing with the application of thio salts in qualitative and quantitative analysis. In view of the strong similarity of selenium to sulphur and the analogous reactions of their salts, the behaviour of the selenium salts has now been investigated for the determination of several metals. A general study of the metals which form insoluble sulphides showed that the selenium compounds behave almost exactly like the corresponding sulphur compounds. Those which form thio salts also form soluble seleno salts with excess of sodium selenide and these are decomposed by excess of acid with the complete precipitation of the corresponding selenides. In other cases insoluble selenides are directly precipitated like the sulphides. The main differences between the compounds of sulphur and selenium lie in the greater toxicity of hydrogen selenide and in the greater contamination of the selenide precipitates with the selenium formed by atmospheric oxidation of sodium selenide. If sodium sulphide is prepared below 5° and precipitation is carried out in ice-cold solutions, the oxidation of sodium sulphide with precipitation of sulphur is negligible. But although the oxidation of sodium selenide is reduced at a low temperature, considerable quantities of selenium are still found in the selenide precipitates. Hydrogen selenide is a colourless gas which produces dryness and a pungent and painful sensation on coming in contact with mucous membranes; its smell is similar to hydrogen sulphide. A specially devised apparatus of the type shown below is therefore necessary.

For sodium selenide to be useful for the determination of metals, atmospheric oxidation of sodium selenide must be prevented both in the preparation of the reagent and during its use as a precipitant. Acceptable results can be obtained by maintaining an atmosphere of carbon dioxide or nitrogen in the bottles in which sodium selenide is prepared and the metallic selenides are precipitated provided that care is taken to prevent sodium selenide coming in contact with air. The slightest exposure to air results in contamination with selenium, but this can be removed by washing with carbon disulphide. The precipitated selenide which remains behind can be weighed in a pure form after washing with alcohol and ether successively and drying in a vacuum desiccator.

As an example of what happens when metals are determined as selenides by adopting ordinary precautions to prevent oxidation, arsenic was precipitated as the selenide (As_2Se_5); a positive error of 0.3–0.4% was obtained when 20–45 mg of arsenic was precipitated.

The prevention of oxidation by ordinary methods requires extreme care, hence it was considered desirable to devise an apparatus (Fig. 1) in which (*a*) the whole procedure could be carried out without contact with air, (*b*) the hydrogen selenide formed could be removed without contaminating the surrounding atmosphere and (*c*) the temperature of the solutions could be maintained between 5–10°.

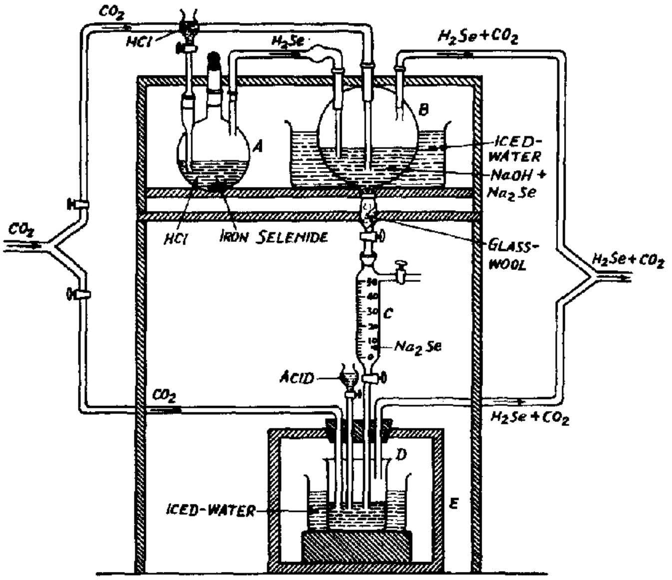

Fig. 1. Apparatus for precipitating selenides.

The following points should be noted with regard to the determination of metals as selenides:

(*1*) The selenides are precipitated by the addition of excess of acid to seleno salts without the heating which is necessary for sulphides.

(*2*) Filtration of the selenides is easier than that of sulphides.

(*3*) All selenides can be weighed after washing with distilled water, alcohol and ether successively and drying in a vacuum desiccator; no heating has been found necessary so far.

It can be seen, therefore, that the selenides provide a more convenient and quicker method of determining metals than sulphides.

Obviously, the apparatus described can be employed for the quantitative precipitation of any metal where oxidation by air interferes.

EXPERIMENTAL

Apparatus (see Fig. 1)

Hydrogen selenide is generated in flask A by adding concentrated hydrochloric acid to ferrous selenide and is passed into the sodium hydroxide solution in flask B, which is maintained at 5–10° by placing it in iced water. Flask B is fitted with three tubes: the first to remove air in the flask by passing carbon dioxide, the second to conduct hydrogen selenide from flask A, and the third to remove the excess of hydrogen selenide by means of a long rubber tube which leads out of the laboratory.

The sodium selenide solution is placed in burette C and a measured volume is then added to the beaker D containing the cold metallic salt solution. The beaker is placed in a trough containing iced water within a cabinet E which is also fitted with (*1*) a thistle funnel for adding measured quantities of acid, (*2*) a tube for conducting carbon dioxide into the beaker (which removes air from the cabinet and stirs the solution) and (*3*) a tube for removing the hydrogen selenide formed by the addition of acid to the seleno salts. The whole operation is thus carried out easily without any contact with air until the insoluble selenide has been precipitated and is ready for filtration, washing and weighing.

METHODS

Preparation of hydrogen selenide

Alternate layers of iron filings (obtained by drilling soft iron) and powdered selenium were placed in a Rose crucible which was then heated to 500–650° for about an hour. The resulting cooled mass of ferrous selenide was removed and powdered and a portion was placed in flask A, from which all air had been displaced by carbon dioxide. On adding concentrated hydrochloric acid through the thistle funnel a steady stream of hydrogen selenide was evolved after a few minutes and conducted into flask B.

Preparation of sodium selenide

After flask B had been freed from air by carbon dioxide, 150–200 ml of a 2 *N* sodium hydroxide solution (E. Merck) was introduced and cooled to a temperature of 5–10°. Hydrogen selenide was then passed into this solution for 5–7 min. The hydrogen selenide was evolved slowly and bubbled through the solution in flask B forming sodium selenide. If the temperature of the solution fell below 5° the sodium selenide tended to precipitate as white crystals and clogged the tube leading to burette C. The same thing happened if the concentration of alkali was much above 2 *N*. Some glass wool was placed at the bottom of flask B to catch any solid sodium selenide formed. If the temperature rose much above 10°, the sodium selenide tended to decompose imparting a reddish colour to the solution. A temperature of 5–10° gave the best conditions. The excess of hydrogen selenide, after the preparation of sodium selenide, was removed by passing carbon dioxide through the flask B into the long rubber exit tube.

Precipitation of selenides

A measured volume of the metallic salt sample solution was placed in the beaker D which was cooled to about 10°. After the air in the cabinet had been removed by passing carbon dioxide, a measured volume of the sodium selenide solution was added from burette C (provided with an outlet tube at the top to allow displacement of the carbon dioxide and introduction of sodium selenide). The solution of the seleno salt was stirred for a few seconds with carbon dioxide and a measured volume of hydrochloric acid or acetic acid was then added through a thistle funnel to decompose the seleno salt (if formed) and precipitate the insoluble selenide. The insoluble selenide was quickly and completely precipitated in an easily filterable form without heating. A current of carbon dioxide was then passed into the mixture for stirring and to remove completely the hydrogen selenide evolved. The beaker was then removed from the cabinet, the mixture was filtered through a sintered glass crucible (porosity G 4) and the precipitate was washed successively with water, alcohol and ether, sucked dry for 15 min at the filter pump, dried in a vacuum desiccator for about 30–35 min and weighed.

Materials

The materials used in the various determinations were usually obtained from E. Merck, B.D.H. (AnalaR), or Kahlbaum, and the solutions prepared were carefully standardized by reliable methods.

It was considered desirable to make a thermogravimetric study of the selenides precipitated in order to obtain definite information regarding the correct conditions for weighing. The results so obtained are described below. A standard Stanton Thermobalance was used; details of its working have been given previously[3]. The reagents used and the methods followed in preparing precipitates for thermogravimetric studies were the same as in the gravimetric determination.

Determination of elements

Arsenic

Solutions of sodium arsenate were prepared and standardized by Volhard's method[4] or by the sodium sulphide method[2]. Aliquots of the solutions were then treated with excess of the freshly prepared 2 *N* sodium selenide solution, about 25 ml of the alkali selenide solution being required for every 50 mg of arsenic. The clear solution was then treated with sufficient hydrochloric acid (12 *N*) to neutralize the alkali and to give a final concentration of approximately 6 *N* hydrochloric acid. The mixture was left in the ice-cold water and stirred thoroughly with carbon dioxide. The precipitate of arsenic selenide, brick-red in colour, was then filtered and treated as in the above general method. The weight of the precipitate corresponded to the formula As_2Se_5. In some experiments the precipitate of arsenic selenide was also washed with carbon disulphide but there was no change in weight, which shows that no precipitation of free selenium occurred.

Typical results obtained by this procedure are shown in Table I.

The air-dried sample of arsenic pentaselenide gave a horizontal level up to 410°. From this temperature the selenide began to sublime and the sublimation was com-

TABLE I

WITH 2 *N* SODIUM SELENIDE REAGENT

Arsenate solution (*ml*)	*Reagent added* (*ml*)	*12 N HCl added* (*ml*)	*Weight of ppt.* As_2Se_5 (*g*)	*As found* (*g*)	*As present* (*g*)
25	35	45	0.2512	0.06908	0.06903
25	40	55	0.2513	0.06911	
25	35	50	0.2512	0.06908	
20	18	25	0.1280	0.03521	0.03520
20	20	30	0.1280	0.03521	
20	20	35	0.1281	0.03523	
10	15	20	0.1003	0.02758	0.02754
10	15	20	0.1003	0.02758	
10	10	15	0.1002	0.02755	

pleted at 550°. At this temperature the crucible was found to be empty (Fig. 2).

Tin

A pure sample of metallic tin was dissolved in concentrated hydrochloric acid and oxidized with bromine and the solution of stannic chloride was standardized by the cupferron[5], ammonia[4] or the sodium sulphide method[1]. Aliquots of this solution were treated with ammonium hydroxide until a white precipitate of stannic hydroxide appeared and then with excess of the selenide reagent. This gave a brownish-yellow solution of sodium seleno-stannate, which was then decomposed by excess of 4 *N* hydrochloric acid to form a reddish brown precipitate. The mixture was cooled in ice-cold water and the precipitate of tin selenide filtered and treated as in the general method. The weight of the precipitate corresponded to the formula $SnSe_2$.

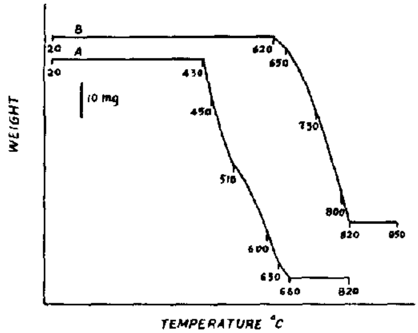

Fig. 3. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, antimony pentaselenide; B, silver selenide.

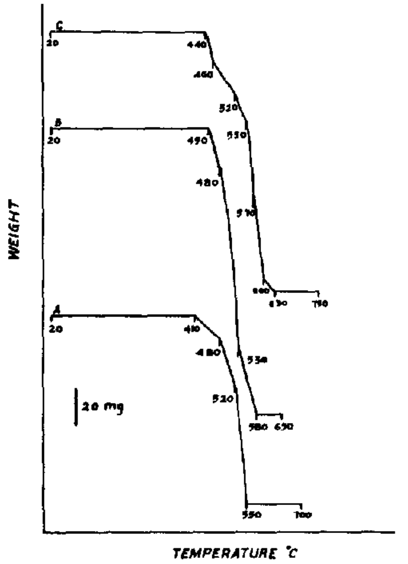

Fig. 2. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, arsenic pentaselenide; B, rhenium heptaselenide; C, mercuric selenide.

The solution of sodium seleno-stannate should be decomposed with sufficient 4 *N* hydrochloric acid to give a final acidity of 1–2 *N*. If more acid is used the precipitate tends to pass through the filter.

Antimony

A solution of potassium hydrogen antimonate was prepared and standardized by reduction with mercury[6] and titration with potassium bromate[7] or by the sodium sulphide method[2]. Aliquots of this solution were treated with the selenide reagent and the seleno salt formed was decomposed with an excess of 4 *N* hydrochloric acid. The mixture was then cooled and the brown precipitate of antimony selenide was filtered, and treated as in the general procedure. The weight of the precipitate corresponded to the formula Sb_2Se_5.

Antimony cannot be determined as selenide from antimony potassium tartrate solution, because sodium selenide forms metallic selenium with sodium tartrate.

An air-dried sample of antimony pentaselenide gave a horizontal up to 430° and then lost weight. The loss was complete at 660° and a horizontal was obtained beyond 660° corresponding to Sb_2O_4. The antimony formed by the decomposition of the pentaselenide was oxidized immediately to Sb_2O_4. The behaviour of antimony selenide therefore corresponded to that of the sulphide[3] (Fig. 3).

Platinum

Solutions of platinic chloride were standardized by reduction to metal with formic acid[8] or by the sodium sulphide method[2]. Aliquots were neutralized with a cold sodium hydroxide solution and treated with the selenide reagent. The solution containing the seleno salt was acidified with a large excess of acetic acid, stirred well with carbon dioxide, cooled in iced water and treated with about 5 g of ammonium acetate. (If hydrochloric acid was used instead of acetic acid the precipitate tended to pass through the filter). The black precipitate of platinum selenide was filtered at a low pressure and treated as in the general procedure. The ratio of the weight of the metal to that of the precipitated selenide was always found to be 0.4403 which corresponds exactly to the formula $PtSe_2 \cdot 5\ H_2O$.

An oven-dried sample of platinum selenide lost weight from 220° to 500°. From 500° to 700° there was a horizontal corresponding to the weight of the metal (Fig. 4).

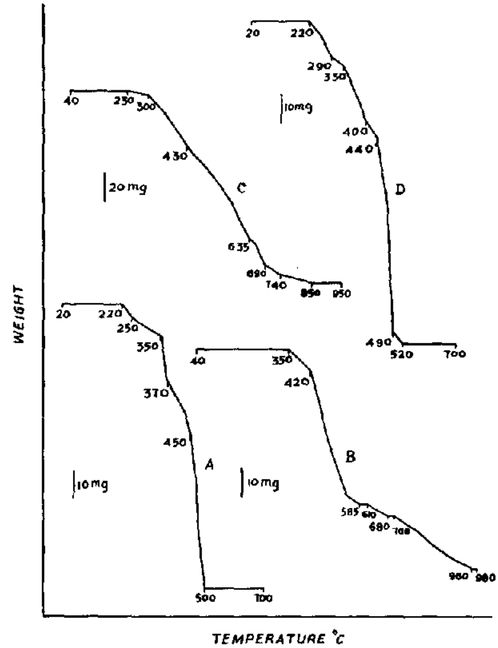

Fig. 4. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, platinum selenide; B, palladium selenide; C, rhodium selenide; D, ruthenium selenide.

Ruthenium

Ruthenium can be precipitated as metal[9] from an alkaline solution by boiling with alcohol. The precipitated metal is ignited and cooled in a current of hydrogen and weighed. If ruthenium selenide is precipitated by treating the solution with sodium selenide and acetic acid successively it can be weighed directly after washing with alcohol and ether, and the whole determination is completed in about 3 h.

Solutions were prepared and standardized by the sodium sulphide method[2]. Aliquots of the solution were made slightly alkaline with a cold solution of sodium hydroxide, then treated with a large excess of the selenide reagent followed by acetic acid in excess and about 10 g of ammonium acetate. The precipitate was then treated as usual. The ratio of the weight of the metal to that of the precipitate was always found to be 0.4267 which corresponds exactly to the formula $Ru_2Se_3 \cdot 2\ H_2O$.

An oven-dried sample of ruthenium selenide lost weight from 220° to 520°. From 520° to 700° there was a horizontal which corresponded to the weight of the metal. Because of spurting, the experiment was carried out in a partly covered crucible (Fig. 4).

Palladium

Solutions of palladium chloride were prepared in dilute hydrochloric acid and standardized by the dimethylglyoxime method[10] or the sodium sulphide method[2]. Aliquots were neutralized with ammonium hydroxide and treated with the selenide reagent. The determination was then completed as for platinum. The weight of the black precipitate of palladium selenide corresponds to the formula PdSe.

The air-dried sample of palladium selenide gave a horizontal up to 350° and then lost weight. There were two horizontals from 585° to 610° and 680° to 700°. These horizontals did not correspond to any exact formula. The loss in weight continued up to 960° after which there was a horizontal up to 980° corresponding to the weight of the metal (Fig. 4).

Rhodium

In all the known methods for the determination of rhodium, except the sodium sulphide method[2], the precipitate must be ignited and cooled in a current of hydrogen before being weighed. A careful study of the behaviour of rhodium salts with sodium selenide and acetic acid has shown that the precipitate of the selenide, after suitable treatment, can be weighed directly.

A solution was prepared by dissolving rhodium chloride in dilute hydrochloric acid and standardized by the formic acid method[11] or by the sodium sulphide method[2]. The determination as selenide was done in the same way as for palladium. The ratio of the weight of the metal to that of the precipitate was always found to be 0.3001 which corresponds exactly to the formula $Rh_2Se_3 \cdot 3\ H_2Se$.

The air-dried sample of rhodium selenide gave a horizontal up to 230° and lost weight from 230° to 850°. From 850° to 950° there was a horizontal corresponding to the weight of the metal. Because of slight spurting, the experiment was carried out in a partly covered crucible (Fig. 4).

Rhenium

Rhenium forms, on treatment with sodium sulphide, a thio salt[2] which decomposes on acidification to precipitate the heptasulphide. Similarly, rhenium forms, on treatment with sodium selenide, a seleno salt which decomposes on acidification to yield heptaselenide. Treatment with acetic acid and ammonium acetate fails to decompose the seleno salt completely and gives low results, but treatment with excess of concentrated hydrochloric acid is satisfactory.

A solution of perrhenate was standardized by the sulphide–nitron method[12] or the sodium sulphide method[2]. Aliquots were treated with the selenide reagent, followed by a large excess of 12 N hydrochloric acid. The selenide was completely precipitated without heating (unlike sulphide[2]) and the precipitate settled easily on cooling in ice-cold water. The black precipitate of the selenide was filtered, washed, dried and weighed as in the case of platinum. Its weight corresponded to the formula Re_2Se_7.

The air-dried sample of rhenium heptaselenide gave a horizontal up to 450°. There was a steady loss in weight from 450° to 580° and at 580° the crucible was found to be empty (Fig. 2).

Mercury

Solutions of mercuric chloride were standardized by VOLHARD's method[13] or by the sodium sulphide method[2]. Aliquots were treated with ammonium hydroxide until a slight turbidity appeared and then with an excess of the selenide reagent. The formation of the seleno salt of mercury with sodium selenide required a large excess of reagent and vigorous shaking. The mixture was acidified with 6 N hydrochloric acid (final acidity 3 N) and cooled in ice-water. The black precipitate of mercuric selenide was then filtered and treated as in the general procedure. Its weight corresponded to the formula HgSe.

The air-dried sample of mercuric selenide was stable up to 440°. A rapid loss in weight then ensued up to 630° when the crucible was found to be empty (Fig. 2).

TABLE II

DETERMINATION OF METALS AS SELENIDES

Metal	*Amount of metal (g)*	*Error %*
Arsenic	0.0690–0.0176	+0.03–+0.20
Antimony	0.0693–0.0181	+0.03–+0.20
Tin	0.0783–0.0250	+0.05–+0.30
Platinum	0.0420–0.0105	+0.05–+0.35
Palladium	0.0628–0.0230	+0.10–+0.30
Rhodium	0.0285–0.0072	+0.07–+0.35
Ruthenium	0.0592–0.0148	+0.06–+0.25
Rhenium	0.0347–0.0131	+0.10–+0.35
Mercury	0.1479–0.0300	+0.06–+0.30
Silver	0.0874–0.0262	+0.04–+0.25
Gold	0.0595–0.0149	+0.02–+0.10

TABLE III

METAL SULPHIDES AND SELENIDES FORMED

Salt	*Arsenic*	*Antimony*	*Tin*	*Rhenium*	*Mercury*	*Silver*	*Platinum*	*Palladium*	*Rhodium*	*Gold*	*Ruthenium*
Thio salt	As_2S_5	Sb_2S_5	$SnS_2 \cdot 2\,H_2O$	Re_2S_7	HgS	Ag_2S	$PtS_2 \cdot 5\,H_2O$	$PdS \cdot 2\,H_2O$	$Rh_2S_3 \cdot 3\,H_2S$	Au_2S_3	$Ru_2S_3 \cdot 2\,H_2O$
Seleno salt	As_2Se_5	Sb_2Se_5	$SnSe_2$	Re_2Se_7	HgSe	Ag_2Se	$PtSe_2 \cdot 5\,H_2O$	PdSe	$Rh_2Se_3 \cdot 3\,H_2Se$	$Au_2Se_3 \cdot H_2Se$	$Ru_2Se_3 \cdot 2\,H_2O$

Silver

Solutions of silver nitrate were standardized by VOLHARD's method[11] or by weighing as silver chloride[14]. Aliquots were treated with ammonium hydroxide until a clear solution was obtained, and then with an excess of the selenide reagent, stirred well and cooled in ice-cold water. The brownish-black precipitate was filtered and treated as in the general procedure. The weight corresponded to the formula Ag_2Se.

The air-dried sample of silver selenide gave a horizontal up to 620°. A rapid loss in weight followed up to 820°. The horizontal from 820° corresponded to the weight of the metal (Fig. 3).

Gold

The well-known method for the gravimetric determination of gold depends on reduction and weighing as the metal. The reduction method takes 6–12 h, depending on the reducing agent used; the method described below requires 3 h and gives results which are as accurate as those obtained by reduction.

Solutions were standardized by precipitating the metal either with sulphur dioxide[15] in an acid medium or with hydrogen peroxide[11] in an alkaline medium. Aliquots were made alkaline with a cold solution of sodium hydroxide, treated with the selenide reagent and shaken thoroughly. An excess of 6 *N* hydrochloric acid was then added and the black selenide was treated as in the general procedure. The ratio of the weight

TABLE IV

Weight of Ag_2Se taken (mg)	*Weight of Ag calculated (820°–950°) (mg)*	*Weight of Ag from graph (820°–950°) (mg)*
190	140	140
427	313	312
118	57	56
232	112	110
Weight of $PtSe_2 \cdot 5\,H_2O$ taken (mg)	*Weight of Pt calculated (500°–700°) (mg)*	*Weight of Pt from graph (500°–700°) (mg)*
315	139	140
165	72	73
Weight of PdSe taken (mg)	*Weight of Pd calculated (960°–980°) (mg)*	*Weight of Pd from graph (960°–980°) (mg)*
200	115	116
213	123	124
Weight of $Ru_2Se_3 \cdot 2\,H_2O$ taken (mg)	*Weight of Ru calculated (520°–700°) (mg)*	*Weight of Ru from graph (520°–700°) (mg)*
194	83	81
162	69	67
Weight of $Rh_2Se_3 \cdot 3\,H_2Se$ taken (mg)	*Weight of Rh calculated (850°–950°) (mg)*	*Weight of Rh from graph (850°–950°) (mg)*
216	65	66
197	59	60

of the metal to that of the precipitate was found to be 0.5538 which corresponds exactly to the formula $Au_2Se_3 \cdot H_2Se$.

The amounts of metal involved in the determinations and the percentage errors are shown in Table II. The compounds formed by sulphides and selenides in the case of different metals are given in Table III for comparison.

The thermogravimetric studies showed that the precipitates of As_2Se_5, Re_2Se_7 and HgSe sublime at a particular temperature, while Sb_2Se_5 is converted to Sb_2O_4 and Ag_2Se, $PtSe_2 \cdot 5\ H_2O$, PdSe, $Rh_2Se_3 \cdot 3\ H_2Se$ and $Ru_2Se_3 \cdot 2\ H_2O$ are converted to their metals (as in the case of the corresponding sulphides[3]).

The weights calculated and those actually obtained on heating Sb_2Se_5, Ag_2Se, $PtSe_2 \cdot 5\ H_2O$, PdSe, $Rh_2Se_3 \cdot 3\ H_2Se$ and $Ru_2Se_3 \cdot 2\ H_2O$ are given in Table IV.

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SUMMARY

The gravimetric determination of metals as selenides is proposed. Owing to the rapid atmospheric oxidation of sodium selenide and the toxic nature of hydrogen selenide, special apparatus is required. The methods are analogous to precipitation of sulphides. Arsenic, tin, antimony, platinum, ruthenium, palladium, rhodium, rhenium, mercury, silver and gold can be determined. The thermolysis of precipitates formed with arsenic, antimony, mercury, silver, rhenium, platinum, ruthenium, palladium and rhodium has been studied.

RÉSUMÉ

Les auteurs ont effectué une étude sur le dosage gravimétrique de métaux sous forme de séléniures. L'arsenic, l'étain, l'antimoine, le platine, le ruthénium, le palladium, le rhodium, le rhénium, le mercure, l'argent et l'or ont pu être ainsi dosés.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die gravimetrische Bestimmung von Arsen, Antimon, Zinn, Platin, Ruthenium, Palladium, Rhodium, Rhenium, Quecksilber, Silber und Gold als Selenide und das thermolytische Verhalten dieser Selenide.

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