and 5 amperes. This rate falls off greatly with increase in time and wavelength and with decrease in current. This is true of all mercury lamps, so that the shorter the wave length used, the more advantageous is the ease of renewal of the open type.

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THE SEPARATION OF SELENIUM AND TELLURIUM

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Jannasch and Müller[1] in 1898 have claimed that selenium and tellurium can be completely separated in the presence of concd. hydrochloric acid by boiling with hydroxylamine hydrochloride. Their procedure is to dissolve a mixture of the oxides in concd. hydrochloric acid in an Erlenmeyer flask, add 8-10 g. of hydroxylamine hydrochloride and boil for an hour under a reflux condenser. The method has not come into general use, although recently Moser and Miksch[2] studied the method and reported that it is accurate but the precipitation is too slow and too much hydroxylamine hydrochloride is required.

In previous papers[3] the authors have shown that, when sulfur dioxide is added to the hydrochloric acid solution of selenium dioxide, the first stage of the reaction consists in the reduction of tetravalent selenium to selenium monochloride which is volatile when the solution is warmed. Indeed, in the presence of sulfuric acid this reduction makes an admirable method for the preparation of pure monochloride.[3]

That other reducing agents reduce selenium dioxide in hydrochloric acid to the monochloride can be very easily demonstrated. A solution of selenium dioxide in concd. hydrochloric acid, when treated with a warm reducing agent, will assume at first a yellow, then a deep red color, and in a few minutes the monochloride distils. The reducing agents which, when added to selenium dioxide in concd. hydrochloric acid, produce the monochloride are hydrazine hydrochloride, hydroxylamine hydrochloride, sulfur dioxide, metallic tin, aluminum, chromium, manganese, magnesium, iron, cadmium, zinc, lead, arsenic, antimony, cobalt, nickel, bismuth, copper, elementary tellurium, red phosphorus, yellow phosphorus, hydrogen sulfide, cadmium sulfide, zinc sulfide, stannous chloride, ferrous chloride and cuprous chloride. When these reducing agents are added to an excess of selenium dioxide dissolved in hydrochloric acid, the monochloride of selenium is formed. In some cases, as with the active reducing agents, the monochloride forms quickly; in others, it forms slowly. When the

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[1] Jannasch and Müller, *Ber.*, **31**, 2389 (1898).

[2] Moser and Miksch, *Monatsh.*, **44**, 349 (1923).

[3] Lenher and Kao, THIS JOURNAL, **47**, 769, 772 (1925).

reducing agent is in great excess, the monochloride can be reduced to elementary selenium without allowing the monochloride an opportunity to escape when the system is warmed. Such is the case with sulfur dioxide. In quantities insufficient to precipitate the element, sulfur dioxide reduces the tetrachloride to the monochloride, giving the calculated yield of monochloride. When added in great excess even in the presence of concd. hydrochloric acid, reduction to the element takes place. In other words, when sulfur dioxide is slowly added to selenium dioxide in concd. hydrochloric acid and the solution is warmed, selenium monochloride is produced and low results ensue. When used as a precipitating agent, sulfur dioxide must be employed in great excess and in the cold.

With certain of the reducing agents which react slowly (for example, hydroxylamine hydrochloride), selenium monochloride can be produced in large quantities even though the reducing reagent be in great excess.

The formation of selenium monochloride can be made the basis of a very pretty lecture experiment. When selenium dioxide in concd. hydrochloric acid is treated in a test-tube with a small portion of any of the above-mentioned reducing agents and the mixture gently warmed, the monochloride is formed in this acid solution, and a red-brown color appears. At the appearance of the red-brown color of the monochloride, the test-tube is chilled by running water and red, elementary selenium is at once precipitated. This precipitation is due to the hydrolysis of the selenium monochloride in the cold. When this solution is warmed again, the red selenium redissolves in the tetrachloride and, again, when chilled, reprecipitation of selenium takes place. This can be repeated indefinitely.

Hydroxylamine hydrochloride is, of course, only sparingly soluble in concd. hydrochloric acid in the cold; as the solution is warmed, hydrogen chloride escapes, the acid becomes weaker and the hydroxylamine hydrochloride dissolves.

The conditions of the experiments of Jannasch and Müller have been repeated, and the exact details followed as given in their description, using 8–10 g. of hydroxylamine hydrochloride in concd. hydrochloric acid. With knowledge of the formation of the monochloride we have in a short time distilled 9 to 18% of the selenium in a 0.5g. sample through a 90-cm. glass condenser and recovered the selenium from the distilled monochloride.

Another factor to be considered is that when concd. hydrochloric acid solutions are boiled, the strength of the acid is materially weakened, hence boiling such a concentrated acid solution would give a hydrochloric acid of such strength that tellurium would barely be held in solution.

That elementary tellurium, when added to the hydrochloric acid solution of selenium dioxide, forms the monochloride is consistent with the places of these two elements in the electrochemical series. In hydrochloric acid solutions, elementary tellurium added to a hydrochloric acid solution of selenium dioxide in the cold is completely replaced by selenium, going through the intermediate stage of the monochloride. Similarly, tellurium introduced into an aqueous solution of selenium dioxide is slowly replaced by elementary selenium, insoluble tellurium dioxide separating at the same time. It is evident, therefore, that in a reduction process of separation, selenium must, in aqueous solution, precipitate first.

Separation of Selenium and Tellurium in Hydrochloric Acid Solution by Hydroxylamine Hydrochloride

That proper concentration of hydrochloric acid is necessary in separating selenium and tellurium by hydroxylamine is obvious from the experiments described above. In the presence of highly concentrated acid, selenium may be distilled and the results will be low. On the other hand, when the acid is too dilute, the precipitation of the selenium will be much delayed. On long standing in quite dilute hydrochloric acid solution, tellurium dioxide precipitates by the hydrolysis of the chloride. In a concentration of 17% hydrochloric acid (d., 1.085), selenium and tellurium can be separated completely by hydroxylamine hydrochloride.

Procedure.—Half a gram or less of the mixed oxides is dissolved in 35–45 cc. of concd. hydrochloric acid and the solution diluted with water to 100 cc. To this is added 10 cc. of a 25% solution of hydroxylamine hydrochloride and the mixture heated to 90° for four hours. The black selenium formed is transferred to a prepared Gooch crucible, washed with water, then with alcohol, dried at 110° and weighed.

The filtrate is evaporated to 50 cc. on a steam-bath, 15 cc. of a saturated solution of sulfur dioxide is added, followed by 10 cc. of a 15% solution of hydrazine hydrochloride, then 25 cc. more of sulfur dioxide solution. Complete precipitation of the tellurium can be effected by boiling the solution for five minutes. The tellurium is transferred to a Gooch filter, washed with hot water followed by alcohol, dried at 110° and weighed.

TABLE I

RESULTS

No. of detns.	Se taken, g.	Se found, g.	Error Av. dev. of the mean	Te taken, g.	Te found, g.	Error Av. dev. of the mean
16	0.2083	0.2084	±0.0003	0.2106	0.2105	±0.0004
4	.2204	.2203	− .0002	.2106	.2105	± .0003
12	.2204	.2205	± .0003	.0213	.0212	± .0004
9	.0321	.0321	± .0002	.2106	.2106	± .0003

Separation of Selenium and Tellurium in Tartaric Acid Solution by Means of Hydroxylamine Hydrochloride

In the presence of tartaric acid, hydroxylamine hydrochloride completely precipitates selenium but not tellurium.

When 25 cc. of a solution of selenium dioxide containing 8.4320 g. of selenium per liter is treated with 25 cc. of a 25% solution of tartaric acid followed by 50 cc. of water and 10 cc. of a 25% hydroxylamine hydrochloride solution, which is roughly twice the calculated amount required for complete precipitation, heating for four hours on the steam-bath completely precipitates all the selenium in condition suitable for filtration. Inasmuch as the precipitation by hydroxylamine is not instantaneous but much delayed, and requires heat, there is no danger of occlusion, as pointed out in the discussion of the sulfur dioxide method.[3] The selenium is washed with water and then alcohol, and dried at 105–110°. In an average of six determinations, 0.2108 g. of selenium was taken and 0.2107 g. was found; error, —0.0001 g.

In order to ascertain whether the sulfur dioxide-hydrazine method of precipitation of tellurium is applicable in the presence of tartaric acid, a series of experiments has been conducted in which 20 cc. of a solution of tellurium dioxide, containing 23.9850 g. of tellurium per liter, was treated with 25 cc. of a 25% solution of tartaric acid and 50 cc. of water. Ten cc. of concd. hydrochloric acid was added, followed by 15 cc. of a saturated solution of sulfur dioxide, then 10 cc. of a 15% solution of hydrazine hydrochloride and 25 cc. more of a saturated solution of sulfur dioxide. When this was boiled, the tellurium was completely precipitated. It was washed with hot water, the water displaced by alcohol and the substance dried at 105–110°. In an average of three determinations, 0.4797 g. of tellurium was taken and 0.4799 g. was found; error, +0.0002 g.

When the two elements are present together the procedure is as follows.

The mixture of the two oxides is dissolved in the least possible amount of sodium hydroxide solution. A 25% solution of tartaric acid is then added until the tellurium dioxide first precipitated just redissolves, then 25 cc. more is added. The solution is diluted to 100 cc., heated to 90°, 10 cc. of a 25% hydroxylamine hydrochloride solution is added, and the mixture kept at 90° for four hours. The selenium is then completely precipitated and can be washed with hot water and with alcohol, dried at 105–110° and weighed.

The filtrate and washings from the selenium are concentrated to about 50 cc., heated to boiling and treated with 25 cc. of a saturated solution of sulfur dioxide. Ten cc. of concd. hydrochloric acid is added and 15 cc. of a 15% solution of hydrazine hydrochloride. The tellurium that is precipitated is filtered on a Gooch crucible with prepared asbestos mat, washed quickly with hot water, dried with alcohol, heated to 105–110° for a half hour and weighed.

TABLE II

RESULTS

No. of analyses	Se taken, g.	Se found, g.	Error Av. dev. of the mean	Te taken, g.	Te found, g.	Error Av. dev. of the mean
14	0.2108	0.2109	±0.0003	0.1530	0.1532	±0.0002
7	.2450	.2451	± .0001	.1600	.1600	± .0002
4	.0148	.0148	± .0001	.1600	.1600	± .0002
4	.0247	.0247	± .0002	.1600	.1601	± .0001
3	.2579	.2580	+ .0003	.0395	.0397	± .0001
2	.5807	.5805	± .0002	.0223	.0225	+ .0001

It is seen that selenium can be separated perfectly from tellurium in tartaric acid solution by means of hydroxylamine hydrochloride. In our hands the sulfate of hydroxylamine gave uniformly low selenium results; hence, its use was abandoned.

The selenium precipitated from the tartaric acid solution forms with hydroxylamine hydrochloride more slowly than in the sulfur dioxide-hydrochloric acid method. The operation should be carried out on a steam-bath at 90° and the reaction mixture should be allowed to stand for four hours. During this slower precipitation the selenium is precipitated in the black, granular form and is easily filtered and washed.

The dilution of the solution should be about 100 cc., for with volumes greater than 150 cc. there is always danger of incomplete precipitation.

The quantity of tellurium which the solution should contain should not exceed 0.2500 g. In the case of larger amounts of tellurium, the precipitate is so voluminous that there is grave danger that the tellurium will oxidize and give high results.

In the results given above all of the selenium precipitates have been carefully tested for tellurium which, under the conditions of the experiments, has been found to be absent. Should considerable quantities of free hydrochloric acid be present tellurium will always be found in the selenium.

The procedure outlined above possesses the advantage over the older sulfur dioxide-hydrochloric acid method that the selenium requires no special treatment before it is weighed. Further, the two elements can be separated from all of the elements possibly present in solution, except gold, by precipitation with sulfur dioxide and hydrazine hydrochloride. The precipitate, when treated with nitric acid, d. 1.25, gives the selenium and tellurium in the soluble form and leaves the gold, if present, insoluble. The nitric acid solution is evaporated nearly to dryness, a slight excess of sodium hydroxide solution is added and the above procedure followed. The addition of a ferric salt, as recommended by Keller[4] in separating selenium and tellurium from the other metals, is unnecessary.

Separation of Selenium and Tellurium in the Presence of Citric Acid

Citric acid as well as tartaric acid possesses the property of being able to dissolve and hold in solution large quantities of tellurium dioxide. It is a most excellent reagent to prevent tellurium from precipitating when hydroxylamine hydrochloride is used in precipitating selenium,

From solutions of tellurium containing large amounts of citric acid, the procedure of using sulfur dioxide and hydrazine hydrochloride to precipitate tellurium is quite efficient.

The two elements as ordinarily met in analysis or as separated from the other elements by sulfur dioxide and hydrazine are oxidized by nitric acid, d. 1.25, the excess of nitric acid is evaporated and the oxides are dissolved in the least possible excess of sodium hydroxide solution. To this solution is added a sufficient quantity of a 3–5% solution of citric acid to give a volume of 100 cc., and 10 cc. of a 25% solution of hydroxylamine hydrochloride. The solution is then heated to 90° and maintained at that temperature for four hours. The precipitation of selenium is then complete and the element is in the black, granular form adaptable to filtration. It is transferred to a Gooch crucible with asbestos mat, washed with hot water and with alcohol, dried at 105–110° and weighed. The filtrate and washings are evaporated to about 50 cc. and the tellur-

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[4] Keller, This Journal, **19**, 771 (1897); **22**, 241 (1900).

ium is precipitated according to the sulfur dioxide-hydrazine hydrochloride procedure. With this method large amounts of tellurium should not be used, since when more than 0.2 g. of the element is present a weighable increase in weight due to oxidation takes place.

TABLE III

RESULTS

No. of analyses	Se taken, g.	Se found, g.	Error Av. dev. of the mean	Te taken, g.	Te found, g.	Error Av. dev. of the mean
4	0.2579	0.2580	+0.0001	0.1775	0.1775	±0.0001
4	.0148	.0149	+ .0003	.1775	.1776	+ .0001
4	.2579	.2577	− .0001	.0175	.0175	± .0002

In all of the separations described above the selenium precipitates were examined for tellurium, with negative results. The presence of considerable quantities of free hydrochloric acid causes tellurium to be found with the selenium precipitate.

When the sulfate of hydroxylamine was substituted for the hydrochloride in the citric acid separation, we always obtained low results; hence its use was abandoned.

The Separation of Selenium and Tellurium in the Presence of Oxalic Acid

It has been found that oxalic acid, like tartaric and citric acids, has the property of holding tellurium in solution when hydroxylamine hydrochloride is added. The use of oxalic acid, therefore, makes possible the separation of selenium from tellurium when hydroxylamine hydrochloride is the precipitating agent. Only small quantities of tellurium should be present, since large amounts of oxalic acid will actually slowly precipitate small quantities of tellurium dioxide. In this separation, hydroxylamine hydrochloride is the reagent to be used, since the sulfate gives low results for selenium. Free hydrochloric acid is to be avoided as with the tartaric and citric acid methods.

The oxidized elements are just neutralized in the sodium hydroxide solution, then just sufficient cold oxalic acid solution is added to redissolve the tellurium dioxide that first precipitates. The solution is then diluted to 100 cc., heated to 90°, 10 cc. of a 25% solution of hydroxylamine hydrochloride is added and the mixture maintained at 90° for four hours. The precipitated selenium is readily filtered off and washed and dried as usual. The filtrate and washings are concentrated to 50 cc. and the tellurium is precipitated by the sulfur dioxide-hydrazine hydrochloride method.

TABLE IV

SEPARATION OF SELENIUM AND TELLURIUM IN THE PRESENCE OF OXALIC ACID

No. of detns.	Se taken, g.	Se found, g.	Error Av. dev. of the mean	Te taken, g.	Te found, g.	Error Av. dev. of the mean
7	0.2579	0.2580	+0.0001	0.0254	0.0253	−0.0003
4	.0148	.0148	± .0002	.0254	.0253	− .0001
4	.0148	.0148	− .0001	.1253	.1252	± .0003

Lactic acid is not available, since it alone reduces tellurium solutions to the element.

The Separation of Selenium and Tellurium by Hydrazine Sulfate in Tartaric Acid Solution

Pellini[5] has shown that in the presence of tartaric acid, hydrazine sulfate can be used as a reagent to separate selenium from tellurium. Moser and Miksch[2] do not favor the tellurium recovery which is accomplished by precipitation with hydrogen sulfide and subsequent evaporation with nitric acid. This latter treatment can be avoided by the use of sulfur dioxide and hydrazine hydrochloride originally proposed by Lenher and Homberger.[6] A study of the method, made by E. J. Wechter of this Laboratory, showed that the precipitated selenium contained tellurium and also showed that hydrazine hydrochloride was unsuitable for the separation.

The procedure of Pellini is to heat the solution of the oxides in hydrochloric acid with the addition of ammonium tartrate and hydrazine sulfate for two hours at 50–60°. More hydrazine sulfate is then added and the solution is heated at a higher temperature to complete the precipitation of the selenium.

Under these conditions it has been found that the selenium is slow to settle and difficult to filter off. Much better results are obtained by heating the reaction mixture for four hours at 90°.

Determination of Selenium by Means of Hydrazine Sulfate in the Presence of Tartaric Acid

In an average of 3 analyses, 0.5815 g. of selenium was taken, and 0.5816 g. was found; error, −0.0001. Under the same conditions, tellurium alone is not precipitated, but in a mixture of the two elements, the selenium cannot be obtained at this temperature or at boiling, free from tellurium.

When the solution is not heated above 65° and the time of precipitation does not exceed eight hours, the following procedure gives a fair separation.

The two oxides are dissolved in the slightest possible excess of sodium hydroxide solution and treated with 25 cc. of a 50% solution of tartaric acid; hydrazine sulfate is then added and the solution warmed to 60°, after which it is allowed to stand for eight hours at 50°. The tellurium in the filtrate is precipitated by the sulfur dioxide-hydrazine hydrochloride method.

In an average of four determinations, 0.2579 g. of selenium was taken, 0.2573 g. was found; error, —0.0006; 0.2458 g. of tellurium was taken, 0.2452 g. was found; error, ±0.0005.

The method of Pellini is applicable only when the temperature does not exceed 65° and the solution is allowed to stand for eight hours. The volume for precipitation and the amount of tartaric acid present have little effect.

[5] Pellini, *Gazz. chim. ital.*, **33**, 515 (1903).

[6] Lenher and Homberger, THIS JOURNAL, **30**, 387 (1908).

The use of hydrazine hydrochloride or sulfate in the citric or oxalic acid method invariably gives selenium contaminated by tellurium with correspondingly low tellurium results.

Conclusions

It is possible to separate selenium and tellurium in hydrochloric, tartaric or citric acid solution by means of hydroxylamine hydrochloride. The sulfate of hydroxylamine proved to be less satisfactory. The procedure of separation is very simple and is susceptible of wide variations in the details of technique.

Both hydrazine hydrochloride and the sulfate tend to cause precipitation of tellurium with the selenium; this can be avoided in the method of Pellini by proper control of temperature.

By use of oxalic acid, it is possible by means of hydroxylamine hydrochloride to separate selenium from tellurium, but the technique is so highly complicated by minor factors that it is not as satisfactory as the tartaric or citric acid methods.

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A GENERAL THEORY OF SOLVENT SYSTEMS

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Our theory of solution has developed largely, if not entirely, from a study of water solutions. Water is remarkable as being the parent substance of a large number of acids, the ordinary oxygen or aquo-acids, of bases, the metallic oxides and hydroxides, and of salts, the oxy or aquo salts, besides acting as solvent for a long list of non-related acids and salts, such as the hydro-halides and other non-oxygen acids and their salts. Parallel with this behavior of water is the behavior of liquid ammonia, which has been shown by Franklin to be the parent substance of a series of acids, the ammono acids, of bases, the metallic nitrides, imides and amides, and of salts, the ammono salts;[1] like water, ammonia readily acts as solvent for a great many non-related acids and salts, and in addition acts as solvent for many metals and intermetallic salts.[2] Many solvents have been studied with a view to determining the solubility of the well-known acids, bases and salts, their reactivity with one another and with the solvent, and the conductivity of their solutions.[3] But few, aside from water and ammonia, have been considered from the standpoint of the

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[1] Franklin, THIS JOURNAL, **46**, 2137 (1924).

[2] Kraus, *ibid.*, **44**, 1216 (1922).

[3] See, for example, the publications of Walden, Kahlenberg, Naumann, and of Archibald, MacIntosh and Steele.