Studies on the Determination of Selenium and Tellurium. III

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Synopsis

The gravimetric determination of selenium and tellurium were studied. Selenium was determined successfully by reducing it to metallic state with the lower valence titanium, molybdenum and chromium ions reduced with liquid zinc amalgam under the suitable conditions. By the same procedure, tellurium was determined successfully only with chromium, and with titanium and molybdenum, any available procedure has not been found.

I. Introduction

1. In the 1st[1] and 2nd[2] reports, a method of determining selenium and tellurium by reducing and allowing them to precipitate out as metallic states by sulfur dioxide in hydrochloric acid solution, in the presence of perchloric and sulfuric acids was described also. In the present paper, a method of gravimetric determination by reduction and precipitation of selenium and tellurium with those lower valence metallic in such as titanium, molybdenum, chronium reduced with zinc amalgam.

II. Determination of selenium

1. Experimental

Aqueous solution of selenious acid is stable, so that it was used as the sample. For metals to be used in the reduction, titanium, molybdenum or chromium was used. Such metal solution was reduced in a moderate concentration of sulfuric acid solution with liquid zinc amalgam, filtered through a suitable filter paper to remove amalgam granules, the filtrate was added to the solution of selenious acid to be reduced, mixed thoroughly by shaking, and allowed to stand over night. This mixture was filtered through a filtering crucible, and the precipitate was washed consecutively with 3N hydrochloric acid and water, dried at about 105°C, and weighed as metallic selenium.

(i) Reduction with titanium

Titanium solution : Titanium oxide was dissolved in sulfuric acid by heating and diluted to contain about 0.03 g of titanium in 1 ml of the solution. The concentration of sulfuric acid was 11.5N.

(a) Effect of the concentration of hydrochloric acid : Five ml of the titanium solution (Ti, 0.15 g) with 20 ml of water was reduced with liquid zinc amalgam.

(1) H. Gotô, Y. Kakita, Sci. Rep. RITU, A-4 (1952), 28.

(2) H. Gotô, T. Ogawa, Sci. Rep. RITU, A-4 (1952), 121.

On the other hand, hydrochloric acid and water were added to 5 ml of the selenious acid solution (Se, 52.7mg*), the reduced titanium solution was added to it, and the total volume was brought to 90 or 180 ml. After allowing the mixture to stand at a room temperature over night, the precipitate was filtered, dried, and weighed. The results obtained are shown in Table 1, from which it can be seen that practically constant values were obtained when 0.15 g of titanium was used, irrespective of the concentration of hydrochloric acid.

Table 1.

Concentration of HCl (N)	Total volume (ml)	Se found (mg)	Error (mg)
8	90	53.0	+0.3
8	90	52.6	−0.1
6.6	90	53.0	+0.3
6.6	90	53.8	+1.1
4	90	53.1	+0.4
4	90	53.3	+0.6
2.7	90	53.4	+0.7
2.7	90	53.2	+0.5
0	90	53.5	+0.8
0	90	53.8	+1.1
4	180	52.7	0.0
4	180	53.0	+0.3
2.4	180	53.5	+0.8
2.4	180	53.4	+0.7
0	180	53.2	+0.5
0	180	52.8	+0.1

Se taken : 52.7mg, concentration of H_2SO_4 : 0.57N, Ti added : 0.15g

Table 2.

Ti added (g)	Concentration of HCl (N)	Total volume (ml)	Se found (mg)	Error (mg)
0.3	0	180	53.8	+1.1
″	0	180	53.3	+0.6
″	4	90	52.8	+0.1
″	4	90	53.0	+0.3
0.09	8	90	37.9	−14.8
″	8	″	34.1	−18.6
″	4	″	38.0	−14.7
″	4	″	37.8	−14.9
″	1.3	″	35.2	−17.5
″	1.3	″	36.2	−16.5
″	0	″	33.5	−19.2
″	0	″	32.8	−19.9

Se taken : 52.7 mg

(b) Effect of the amount of titanium: Using 10 ml of the titanium solution (Ti, 0.3g), the same experimental procedures as in (a) were carried out. The results, as shown in Table 2, indicated that well-agreeing values were also obtained by the use of a larger amount of titanium.

The same experiments were then carried out with 3 ml of the titanium solution (Ti, 0.09g). As indicated by the results shown together in Table 2, values obtained were lower, pointing out that this amount of titanium is not sufficient for the reduction.

(ii) Reduction with chromium

For chromium, 10 per cent aqueous solution of chrome alum was used. A mixture of 35 or 50 ml of the chrome alum solution and 1.5 ml of sulfuric acid solution (1 : 1) was reduced with liquid zinc amalgam, as in (1) and the following experiments were carried out as in the foregoing, also with various concentrations of hydrochloric acid or with sulfuric acid alone, and the results are shown in Table 3. These results indicate that well-agreeing values are obtained when 35 ml of 10 per cent chrome alum solution is used at 3.6N hydrochloric acid solution but lower values are obtained with a higher concentration of the acid and

* Determined by reduction and precipitation with hydroxylamine.

higher values with lower concentration. When 50 ml of the chrome alum solution was used, almost constant values were obtained at around 3.6N hydrochloric acid solution, and the variation in values with higher or lower concentration of the acid was more marked in this case. In sulfuric acid solution, the values agreed well with about 6N, and the values were higher at a lower concentration.

(iii) Reduction with molybdenum

For molybdenum, 10 per cent aqueous solution of sodium molybdate was used.

(a) To 5 ml of sodium molybdate solution, 10 ml of 2N sulfuric acid and 5 ml of water were added and the mixture was reduced with liquid zinc amalgam as in the foregoing. Experiments were carried out as before with various concentrations of hydrochloric acid. As shown by the results in Table 4, constant values were obtained when 5 ml of 10 per cent sodium molybdate solution was used, irrespective of the concentration of hydrochloric acid.

(b) Relation between the amount of molybdenum and concentration of hydrochloric acid was examined by varying the amounts of sodium molybdate and the concentration of hydrochloric acid. To 4 or 3 ml of 10 per cent sodium molybdate solution, 10 ml of 2N sulfuric acid and 5 ml of water were added and experiments carried out as in the foregoing. As shown by the results in Table 5, fairly well-agreeing results were obtained with 4 ml of 10 per cent sodium molybdate solution at 5.4~7.2N hydrochloric acid, but the values were lower when hydrochloric acid concentration was lower. However, when hydrochloric acid was not present, the precipitate was contaminated and values determined were higher, suggesting occlusion of molybdenum compound in the precipitate. Values were always lower with 3 ml of the molybdate solution, suggesting insufficiency

Table 3.

10% Chrome alum added (ml)	Concentration of HCl (N)	Se found (mg)	Error (mg)
35	7.2	46.9	−5.8
,,	7.2	47.2	−5.5
,,	4.8	51.5	−1.2
,,	4.8	50.6	−2.1
,,	3.6	53.2	+0.5
,,	3.6	53.0	+0.3
,,	2.4	56.6	+3.9
,,	2.4	57.4	+4.7
,,	1.2	61.2	+8.5
,,	1.2	63.9	+11.2
50	6.0	47.8	−4.9
,,	6.0	47.2	−5.5
,,	4.8	47.5	−5.2
,,	4.8	47.3	−5.4
,,	4.2	51.1	−1.6
,,	4.2	51.1	−1.6
,,	3.6	52.9	+0.2
,,	3.6	53.1	+0.4
,,	3.0	57.2	+4.5
,,	3.0	57.1	+4.4
,,	1.8	63.8	+11.1
,,	1.8	63.5	+10.8
,,	6.0*	52.8	+0.1
,,	6.0*	52.4	−0.3
,,	4.2*	55.1	+2.4
,,	4.2*	54.4	+2.7
,,	3.0*	56.6	+3.9
,,	3.0*	56.7	+4.0

Se taken : 52.7 mg, total volume : 100ml,
* concentration of H_2SO_4

Table 4.

Concentration of HCl (N)	Se found (mg)	Error (mg)
7.2	49.1	+0.4
7.2	49.1	+0.4
5.4	49.2	+0.5
5.4	49.7	+1.0
3.6	48.9	+0.2
3.6	49.7	+1.0
2.4	48.8	+0.1
2.4	49.3	+0.6
1.2	49.2	+0.5
1.2	49.4	+0.7
0	49.2	+0.5
0	49.4	+0.7

Se taken : 48.7 mg, total volume : 100 ml, 10% Na_2MoO_4 added : 5 ml

of the reduction agent. The precipitate was also contaminated in the absence of hydrochloric acid and the values were higher.

Table 5.

10% Na$_2$MoO$_4$ added (ml)	Concentration of HCl (N)	Se found (mg)	Error (mg)
4	7.2	49.5	+0.8
"	7.2	49.5	+0.8
"	5.4	48.9	+0.2
"	5.4	48.5	−0.2
"	3.6	43.9	−4.8
"	3.6	43.5	−5.2
"	1.2	43.8	−4.9
"	1.2	43.2	−5.5
"	0	52.1	+3.4
"	0	53.8	+5.1
3	3.6	34.2	−14.5
"	3.6	36.6	−12.1
"	1.2	32.7	−16.0
"	1.2	30.9	−17.8
"	0	51.6	+2.9
"	0	57.3	+8.6

Se taken : 48.7 mg, total volume : 100 ml, concentration of H$_2$SO$_4$: 0.2N

Table 6.

Concentration of HCl (N)	Se found (mg)	Error (mg)
7.2	49.9	+1.2
7.2	49.2	+0.5
5.4	49.5	+0.8
5.4	49.6	+0.9
3.6	49.5	+0.8
3.6	49.4	+0.7
1.2	48.9	+0.2
1.2	49.0	+0.3
0	50.7	+2.0
0	50.9	+2.2

Se taken : 48.7 mg, total volume : 100 ml, 10%Na$_2$MoO$_4$ added : 10ml

Next, the same experiments were carried out with 10 ml of 10 per cent sodium molybdate solution and 20 ml of 2N sulfuric acid (reduction was impossible with 10 ml of the acid, forming a black precipitate during the reduction). The results in Table 6 show that a slightly higher values are obtained in the absence of hydrochloric acid but practically constant values are obtained in the presence of hydrochloric acid, irrespective of its concentration.

2. Results

(i) When Ti^{3+} was used as the reducing agent, over 0.15 g of titanium resulted in complete reduction of about 0.05 g of selenium and the determination of selenium could be made, irrespective of the concentration of hydrochloric acid. The determination was also possible in sulfuric acid solution, in the absence of hydrochloric acid.

(ii) When Cr^{2+} was used as the reducing agent, about 0.05 g of selenium could be quantitatively determined with 35 ml of 10 per cent chrome alum solution at 3.6N solution of the hydrochloric acid and also with 50 ml of the chrome alum solution, at 3.6N hydrochloric acid gave the good results. Similarly, with 50 ml of the chromium solution, the determination was possible in 6N sulfuric acid solution.

(iii) When Mo^{3+} was used as the reducing agent, constant values were obtained with about 0.05 g of selenium and 5 ml of 10 per cent sodium molybdate solution, irrespective of the concentration of hydrochloric acid. When 4 ml of the molybdate solution was used, agreeable results were obtained in 5.4-7.2N hydrochloric acid solution, and when 10 ml of the molybdate solution was used, practically constant values were obtained at any concentration of hydrochloric acid.

III. Determination of tellurium

1. Experiment

Tellurium solution: Metallic tellurium was dissolved in 6N nitric acid, the acid was removed by evaporation of this solution to dryness, and the residue was made alkaline with sodium hydroxide until the precipitate formed was dissolved completely. This alkaline solution was diluted to a definite volume. The experimental procedures were the same as in the case of selenium.

(i) Reduction with titanium

The titanium solution used was similar with that of selenium and the experimental procedures were also the same, using 54.5 mg* of tellurium. The results, as shown in Table 7, indicated very low values and the higher the concentration of hydrochloric acid became, the lower the value. No precipitation occurred with 8N hydrochloric acid. It was therefore seen that determination of tellurium by reduction and precipitation with titanium was impossible.

(ii) Reduction with molybdenum

As in the case of selenium, 10 per cent aqueous solution of sodium molybdate was used to carry out the same experiments. To 5 ml of 10 per cent sodium molybdate solution, 10 ml of 2N sulfuric acid was added and reduced. Under the condition that 0.0545g of tellurium was added, the total volume brought to 100 ml and hydrochloric acid was not added, the quantitative determination was impossible due to too large an amount of precipitate by molybdenum. In a similar experiment, using 20 ml of 2N sulfuric acid, precipitation failed to form. These facts showed that it is impossible to use molybdenum as the reducing agent.

(iii) Reduction with chromium

10 per cent aqueous solution of chrome alum was used as in the case of selenium.

(a) Effect of the concentration of hydrochloric acid: 50 ml of 10 per cent chrome alum solution and 1.5 ml of sulfuric acid (1:1) was reduced with liquid zinc amalgam and the same experiments were carried out with various concentrations of hydrochloric acid. As shown from the results in Table 8, well-agreeing results were obtained at less

Table 7.

Concentration of HCl (N)	Se found (mg)	Error (mg)
8.0	—	—
8.0	—	—
4.0	0.5	−54.0
4.0	0.7	−53.8
1.3	7.1	−47.4
1.3	7.8	−46.7
0.6	28.9	−25.6
0.6	30.5	−24.0
0	27.8	−26.7
0	27.0	−24.5

Te taken: 54.5 mg, total volume: 90 ml, Ti added: 0.155 g, concentration of H_2SO_4: 0.55N

Table 8.

Concentration of HCl (N)	Se found (mg)	Error (mg)
0	55.2	+0.7
0	55.4	+0.9
1.2	55.0	+0.5
1.2	55.2	+0.7
2.4	54.3	−0.2
2.4	54.8	+0.3
3.6	55.0	+0.5
3.6	55.1	+0.6
4.2	52.9	−1.6
4.2	53.2	−1.6
5.4	50.3	−4.2
5.4	47.6	−6.9

Te taken: 54.5 mg, total volume: 100ml, 10% chrome alum added: 50 ml, concentration of H_2SO_4: 0.27N

* Determined with hydroxylamine and sulfur dioxide.

than 3.6N of hydrochloric acid concentrations, and a slightly lower values at more than 4.2N.

(b) Effect of the amount of chromium : Experiments were carried out, using various amounts of 10 per cent chrome alum solution. The results obtained are shown in Table 9, from which it is seen that values are lower with less than 35 ml of 10 per cent chrome alum solution but agree well with more than 50 ml.

Table 9.

10% Chrome alum added (ml)	Se found (mg)	Error (mg)
25	44.0	−10.5
25	43.6	−10.9
35	52.7	−1.8
35	50.6	−3.9
50	55.2	+0.7
50	55.4	+0.9
65	54.8	+0.3
65	55.4	+0.9

Te taken : 54.5 mg, total volume : 100ml, HCl was not added.

2. Results

(i) It was impossible to quantiatively determine tellurium by reduction and precipitation with Ti^{3+} or Mo^{3+} as the reducing reagent.

(ii) When Cr^{2+} was used as the reducing agent, with about 0.05 g of tellurium, 50 ml of 10 percent chrome alum solution reduced with zincamalgam and lower than 3.6N hydrochloric acid, well-agreeing results were obtained, while lower values were obtained with less than 35 ml of chrome alum.

Summary

(1) A method of gravimetric determination of selenium and tellurium was studied in which these elements were precipitated in metallic state by reduction with titanium, molybdenum, or chromium reduced with liquid zinc amalgam.

(2) When titanous ion was used, suitable amount of titanium made it possible to determine selenium, irrespective of the concentration of hydrochloric acid, or in sulfuric acid solution.

(3) When chromous ion was used, selenium could be determined with around 3.6N hydrochloric acid or in 6N sulfuric acid.

(4) When molybdenum reduced was used, selenium could be determined at any concentration of hydrochloric acid.

(5) It was impossible to determine tellurium by using titanium or molybdenum reduced as the reducing agent.

(6) Tellurium could be determined with chromous ion as the reducing agent at less than 3.6N of hydrochloric acid.