Separation of Selenide Constituents from Selenide Samples Containing Elemental Selenium

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The valence state analysis to determine selenide in mixtures of selenide, elemental selenium, selenite, and selenate compounds was devised by the selective volatilization of selenium as its hydride. As the optimum conditions of the reaction, 6 M (this unit is defined to 1 M=1 mol dm^{-3} as below.) hydrochloric acid solution was dropped into the mixture and the hydrogen selenide gas generated was absorbed in a solution of sodium hydroxide and hydrogen peroxide. The optimal reaction temperature was found to be 170 °C for 40 min using nitrogen as the carrier gas. Utilizing this method, the fluctuation of the oxidation state of selenium was observed during the storage of zinc selenide samples.

The oxidation state of selenium in the lithosphere, hydrosphere, and atmosphere, selenium is mainly classified into the following species; sexivalent, quadrivalent, elemental, minus bivalent, and organically complexed species such as selenate, selenite or selenium dioxide, red amorphous or gray metallic selenium,[1] selenide, and selenomethyonine,[2] respectively.

Although numerous methods for the total analysis of selenium in rock, soil, and sediment samples have been devised. The analysis of the oxidation state of selenium in powdered solid samples has rarely been reported. A method to separate the high valent species of selenium (sexivalent and quadrivalent) from the low valent species (elemental and minus bivalent) in sediment samples was deviced by Terada *et al.*[3] Utilizing a chemical leaching method,[4] the high and low valent species of selenium in marine core sediments with its core depth were analysed by Tamari.[5]

In this work, the reaction conditions in order to determine selenium after separating selenide constituents as the gas of hydrogen selenide from the powdered samples containing elemental selenium, selenite, and selenate were investigated in detail. This study establishes the optimum conditions for the generation of the hydride and its subsequent trapping in absorbents.

Experimental

Reagents and Apparatus. Standard samples of selenide were prepared as follows. Selenide standard was prepared by mixing 0.02 g of zinc selenide powder with 1 g of silica powder in an agate mill for 10 min, and the mixture homogenized by quartering four times.[6] After this preparation, total selenium content of the selenide standard was determined to be 10.04±0.95 μg/mg.[7] Approximately 10 mg of this standard was used for experiments.

Silica powder was used to dilute the selenide standard. Fine quarts powder to pass through the sieve of 100 mesh size was taken in a beaker, and boiled with the solution of 6 M hydrochloric acid. The powder was filtered with a membrane filter (pore size: 3 μ) and rinsed with water, then dried at 110 °C.

The apparatus designed for the generation of hydrogen selenide and the collection of its hydride, is shown in Fig. 1. As can be seen in this figure, a funnel and two traps were connected to a reactor.

All chemicals used were analytical reagent grade; the other reagents and apparatus have been reported by Tamari *et al.*[8]

Recommended Procedure. About 10 mg of a sample was placed in the reactor (see Fig. 1), and 20 cm^3 of 6 M hydrochloric acid solution were added to the funnel. The mixed solution of 2.5 cm^3 of 0.1 M sodium hydroxide and 7.5 cm^3 of 30% hydrogen peroxide were placed in the trap vessels. The reactor connected to the funnel and the traps was set in the hole of an aluminium-block adjusted to 170 °C with a hot-plate. The hydrochloric acid solution was dropped into the reactor using a carrier gas of nitrogen. The hydrogen selenide generated was carried with the gas into the absorbent solution. This reaction was subjected to heating for 40 min at 170 °C. After the reaction, the reactor and the traps were disconnected, and each of the traps to which 1 cm^3 of 30% hydrogen peroxide was added was heated on a hot-plate for a few minutes in order to oxidize the selenide. Then, 1 cm^3 of concd nitric acid was added to each vessel from its tube, and the solution was boiled for a few minutes to oxidize to selenate. After cooling, the solution in each trap was placed in a 100 cm^3 or 250 cm^3 measuring flask, and diluted to the mark with water. The solution in the reactor was filtered with a membrane filter (pore size: 3 μ) and the filtrate was diluted with water to 100 cm^3 or 250 cm^3. To the aliquots of the solution, 0.5 cm^3 of 70% perchloric acid solution was added and evaporated until the perchloric acid vapor appeared. Selenium in the sample solution was completely reduced to selenite by boiling for 3 min after the addition of 2 cm^3 of 6 M hydrochloric acid solution. The selenite solution prepared was determined by fluorometry with 2,3-diaminonaphthalene.[8]

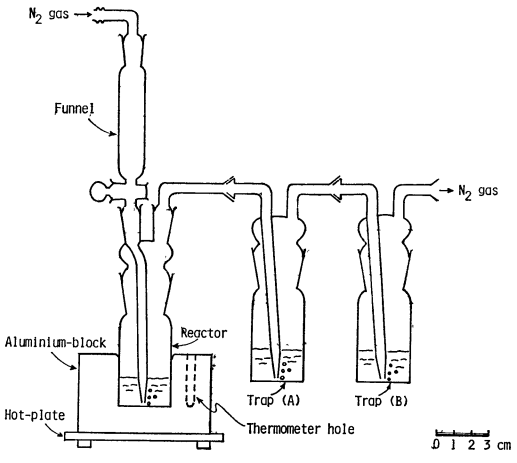

Fig. 1. Apparatus to generate and collect hydrogen selenide.

Table 1. Effect of acid concentration on the generation of hydrogen selenide

Hydrochloric acid (M)	Found selenium[a] (μg)	Ratio of selenium/%[b]		
		Reactor	Trap (A)	Trap (B)
2	85.4	25	75	0
6	91.2	1	99	0
9	100	30	70	0
12	121	37	63	0

a) Total amounts of selenium found in the reactor and traps. b) Percentage ratio of amounts of selenium found in the reactor and traps.

Table 2. Effect of reaction temperature

Reaction temp °C	Found selenium (μg)	Ratio of selenium/%		
		Reactor	Trap (A)	Trap (B)
43—49	73.3	16	84	0
99—103	70.6	27	72	1
170	43.5	7	91	2

Results and Discussion

All experiments were carried out in order to consider the optimum conditions of the reactions based on the generation of hydrogen selenide and its absorption into solutions.

Effect of Carrier Gas. Using air as a carrier gas instead of nitrogen, a considerable amount of selenium remained in the reactor, and red condensates were observed on the wall of the tube between the reactor and the trap (A). The condensate could be red amorphous selenium generated by oxidation of the hydride to elemental selenium. Accordingly the use of nitrogen gas was recommended as the carrier.

Effect of the Concentration of Hydrochloric Acid. Solutions of 2, 6, 9, and 12 M hydrochloric acid were examined. Each 20 cm^3 of the solution was added to the reactor from the funnel under the conditions of the reaction at 170 °C for 40 min and the addition of the solution mixed 19 cm^3 of 0.1 M sodium hydroxide with 1 cm^3 of 30% hydrogen peroxide to each trap. As shown in Table 1, no selenium was found in the trap (B), and the best concentration of the acid solution was considered to be 6 M hydrochloric acid from the results of the data of the recovery of hydrogen selenide in the trap (A).

Effect of Reaction Temperature. The reaction temperature for the generation of hydrogen selenide was examined under the conditions of addition of 6 M hydrochloric acid solution and the same reaction system as described above. Table 2 gives the results of the examination. Since the highest percentage of selenium was found in the trap (A) when the temperature attained 170 °C, this temperature was applied to the experiments below.

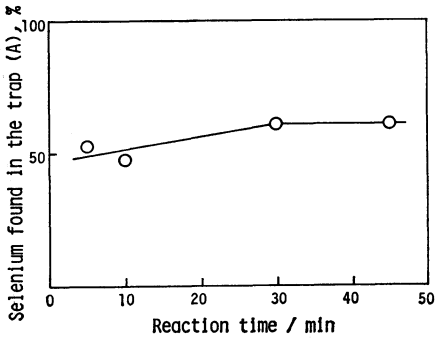

Fig. 2. Effect of reaction time on the generation of hydrogen selenide.

In the case of selenide samples containing selenite and selenate, selenate was reduced to selenite by boiling with the solution of 6 M hydrochloric acid, and the subsequent selenite may be volatilized as selenium tetrachloride above *ca.* 200 °C.[1] In this work therefore it is important to keep the reaction temperature at 170 °C to avoid the volatilization of selenium.

Effect of the Chemical Composition of the Absorbent. Sodium hydroxide solution is generally considered to be an effective absorbent for trapping of hydrogen selenide as well as hydrogen sulfide. However hydrogen selenide can be changed to a more stable chemical form as a red colored precipitate by oxidizing the hydride to avoid the revolatilization of the hydride in the trap. Hence the solutions of hydrogen peroxide and nitric acid were tested for efficiency as oxidant and absorbant of the hydride.

In the chemical system of sodium hydroxide solution containing hydrogen peroxide, the recovery percentage of selenium in the traps was fairly good, whereas in the system of nitric acid solution containing hydrogen peroxide it was relatively low because of the revolatilization of hydrogen selenide due to the acid solution. Futhermore in the latter system, selenium was absorbed into the solution in both the trap (A) and the trap (B). Therefore the fomer system was used for the experiment of hydrogen selenide as an absorbent. Table 3 lists the results of the chem-

Table 3. Effect of the chemical composition of absorbent

Chemical composion of absorbent		Found selenium (μg)	Ratio of selenium/%		
0.1 M NaOH (cm^3)	30% H_2O_2 (cm^3)		Reactor	Trap (A)	Trap (B)
19	1	91.2	1	99	0
15	5	87.2	12	88	0
10	10	108	8	92	0
5	15	107	3	97	0
0	20	87.3	7	93	0

Table 4. Recovery of hydrogen selenide in the recommended procedure

Selenide standard		Selenium found in the trap (A) (%)	Selenium recovery (%)
Taken (mg)	Added (μg)		
11.4	114	90.3	79.2
10.0	100	76.7	76.7
10.9	109	99.4	91.2
12.0	120	104	86.7
10.4	104	81.2	78.1
			Average±standard deviation 82.4±6.3
Elemental selenium added (μg) 1000		0	100
Selenium(IV) added (μg) 100		3	97

ical composition of the absorbent in the system for trapping the hydride. As can be seen in Table 3, no selenium was found in the trap (B) in each absorbent solution, and the solution obtained by mixing 19 cm^3 of 0.1 M sodium hydroxide with 1 cm^3 of 30% hydrogen peroxide was selected as the best absorbent. This was based not only on the results representing the highest value in the trap (A) but also consideration of the post-preparation for the fluorometric determination of selenium with 2,3-diaminonaphthalene.[8]

Effect of Reaction Time. The effect of the reaction time on the generation of hydrogen selenide was investigated under the optimum conditions described above. As is shown in Fig. 2, the constant percentage of selenium in the trap (A) was obtained by reacting for more than 30 min. Hence the reaction for 40 min was undertaken for all the experiments.

Recovery of Hydrogen Selenide in the Recommended Procedure. In the optimum conditions of the reaction for the generation of hydrogen selenide and its trapping in the absorbent, *i.e.*, in the recommended procedure, the experiments for the recovery of selenium were carried out. It can be seen from Table 4 that the selenium recovered was 82.4±6.3%. From the consideration of the homogeneity of selenium in the selenide standard, 10.01±0.95 μg/mg, it was indicated that the coefficient variation of the former value, 7.9%, was included in the latter case, 9.5%. This method was applied to the samples involving the other oxidation state of selenium; 100 μg of selenite and 1 mg of elemental selenium were used for the experiment. As is seen from the results, neither selenite nor elemental selenium was volatilized, and little selenium was found in the trap (A).

Since the proposed method is useful for the determination of selenide, the method will be applied to the samples of the selenium compounds as the valence state analysis of selenide. The authors will report later on the application of this method to the samples.

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