Valence States of Arsenic and Antimony in Sea Water

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A simple and convenient chemical procedure for the determination of As(III), As(V), Sb(III) and Sb(V) by thermal neutron activation analysis is proposed and applied to the study of the valence state of As and Sb in sea water. Immediately after sampling, As(III) and Sb(III) were separated from As(V) and Sb(V) by extracting their diethyldithiocarbamates with chloroform, and then back-extracted into diluted nitric acid. As(V) and Sb(V) in the aqueous phase were collected by thionalide cocrystallization. They were then irradiated for 30 min at a neutron flux of 2×10^{13} n/(cm$^2\cdot$s), and treated in the same manner as described in the previous report.[6] The As and Sb were determined by gamma-ray spectrometry. Sea water has been found to contain 1.56—2.45 μg As/l and 0.37—0.60 μg Sb/l. 80—97% of arsenic and 70—94% of antimony existed as the pentavelent species, only 5—20% as the trivalent species, and the remainder was probably included in suspended matter.

Because arsenic and antimony exist in aqueous solution in two chemical forms, a trivalent and a pentavalent species, it is an interesting problem to investigate the valence state of these elements in sea water. A few reports have been published on the state of arsenic in sea water. Arsenate seems to be much more stable,[1] and Armstrong and Harvey,[2] Gorgy and his cowarkers,[3] Sugawara and Kanamori,[4] Johnson and Pilson[5] studied on the valence state of arsenic in sea water. These studies were useful for the separation and the determination of trivalent and pentavalent arsenic, although their procedures were very complicated. The valence state depends strongly upon the condition of the aqueous solution, and it changes considerably as aqueous conditions change. Accordingly the separation of trivalent and pentavalent species must be done as quickly as possible, because the valence state may be changed during the storage of the sea water sample.

There is no report on the valence state of antimony in sea water.

In a previous report,[6] we proposed a procedure for the neutron activation analysis of arsenic, copper, and antimony in sea water, but the valence states of arsenic and antimony cannot be determined by that method. In the present research, a rapid, simple and convenient procedure for the determination of valence states of arsenic and antimony in sea water was developed. This procedure was based on solvent extraction followed by the neutron activation. Trivalent species were separated from pentavalent species by extraction into chloroform as the diethyldithiocarbamate chelates, and arsenic and antimony in both states were separately collected by thionalide cocrystallization. After neutron irradiation, antimony was precipitated as oxinate and arsenic was coprecipitated with ferric hydroxide, and then the ^{76}As and ^{122}Sb activities were measured. By this procedure, the valence states of micro amounts of arsenic and antimony in aqueous solution can be precisely determined. Some coastal sea water samples were analyzed by this method.

Experimental

Materials. Sodium diethyldithiocarbamate (Na–DDTC): Reagent grade Na–DDTC was used without further purification. To 1 l of sea water 0.3 g of this reagent was added directly.

Thionalide solution, 2% (w/v): 2 g of thionalide (thioglycollic-β-aminonaphthalide) was dissolved in acetone and diluted to 100 ml with acetone. The solution was freshly prepared before use.

Oxine solution, 2% (w/v): 2 g of 8-quinolinol was dissolved in 7 ml of glacial acetic acid and diluted to 100 ml with water.

Sulfuric acid, 3M: Arsenic free sulfuric acid was diluted with water.

Radioisotopes, ^{74}As and ^{124}Sb, were purchased from the Radiochemical Centre, Amersham, England. It was confirmed that the isotopes could not be extracted with DDTC–chloroform, that is, they were the pentavalent species. The trivalent species were obtained by reduction with ascorbic acid.

Apparatus. Gamma-ray spectra were obtained with a well-type 3″×3″ NaI(Tl) scintillation detector connected to a Hitachi RAH-403 400 channel pulse-height analyzer. The activities measurements were measured with a 2″×2″ NaI(Tl) detector and a Hitachi RC-2 scaler.

Extraction Procedure of Arsenic and Antimony Diethyldithiocarbamates. For separation of trivalent species of arsenic and antimony from pentavalent species in sea water, the extraction of arsenic–DDTC and antimony–DDTC chelates using radioactive tracers was studied. Na–DDTC was added to the sea water containing ^{76}As, ^{122}Sb, and ^{124}Sb in trivalent or pentavalent states and 2 μg of the carrier. After the pH was adjusted, the resulting solution was shaken with chloroform. Two milliliters of samples were pipetted from the organic and the aqueous layers, and the activities were measured.

Analytical Procedure. From the experimental results presented below, the following analytical procedure is recommended.

Immediately after the collection of sea water samples, 1 l of sea water was filtered through a 0.45 μm pore-size Millipore filter. After 0.3 g of Na-DDTC was added to the filtered sample, trivalent arsenic and trivalent antimony were extracted as DDTC chelates at pH 2.5—4.0 by shaking successively with 200 ml and 50 ml of chloroform, and then stripped by shaking the organic phase with 50 ml of 3 M nitric acid. After the solution was heated to boil out the dissolved chloroform and diluted to 1 l with redistilled water, the trivalent species were collected by thionalide cocrystallization: after 8 ml of 2% thionalide acetone solution was added to the cooled solution with vigorous stirring, the solutions were boiled for about 30 minutes and then allowed to stand overnight at room temperature. The precipitates were filtered with Millipore filters (pore-size: 0.45 μm) and washed with redistilled water.

After the extraction the aqueous phase was acidified to 0.15 M with sulfuric acid, and pentavalent species remaining in the solution were also collected by the thionalide cocrystallization.

Millipore filters employed for the filtration of sea water samples, the filters including the thionalide precipitates, and the standards were separately packed in polyethylene capsules (8 mm long × 12 mm in diameter), which were placed in a polyethylene rabbit tube, and irradiated for 30 minutes at a thermal neutron flux of 2×10^{13} n/(cm^2·s) in the Kyoto University Reactor.

After cooling for a few hours, the irradiated samples were treated as reported previously.[6]

The oxinates and the ferric hydroxide precipitates were used for the gamma-ray spectrometry of ^{76}As and ^{122}Sb. For the hydroxide precipitate, the 0.55 MeV gamma-ray photopeak following the decay of ^{76}As was counted. For the oxinates precipitate, the decay of the 0.57 MeV photopeak of ^{122}Sb was followed, after ^{64}Cu (0.51 MeV annihilation gamma-rays) had decayed.

Results and Discussion

Redox Behavior of Arsenic in Salt Solution and Sea Water. Oxidation of arsenic(III) was measured by determining arsenic(V) by the molybdenum blue method, and reduction of arsenic(V) was followed by DDTC extraction using the radioactive isotope, ^{74}As(V). The rate of oxidation of arsenic(III) in 0.1 M sodium perchlorate, 0.1 M sodium chloride, and 0.025 M sodium sulfate solutions is shown in Fig. 1. When sodium arsenite (containing 5 mg of arsenic(III)) was dissolved in 1 l of these solutions, the pH of which had been previously adjusted to 8.0—8.5 with sodium hydroxide solution, 20—30% of arsenic(III) was immediately oxidized to arsenic(V). Then the oxidation proceeded slowly and 50—60% of arsenic existed as the pentavalent species after 400 hours standing. Aeration accelerated oxidation.

The oxidation-reduction of arsenic in sea water and artificial sea water are shown in Fig. 2. In artificial sea water, the effect of aeration was not appreciable, and after 400 hours, about 50% of arsenic(III) was oxidized to arsenic(V). The effect of aeration was significant in sea water; about 50% of the arsenic(III), which was added as sodium arsenite (containing 5 mg of arsenic) to sea water (1 l), was oxidized after 400 hours of aeration, but only about 20% was oxidized without aeration.

Curves 3—6 in Fig. 2 show the behavior of arsenic(V) added to sea water. The reduction of arsenic(V) to arsenic(III) may be caused by the decomposition of organic matter in the samples. In sea water which contains very small amounts of organic substances, reduction was not observed even after standing for 400 hrs (as shown by curve 6), and the same result was obtained in artificial sea water or the salt solutions described above.

In the case of antimony, decisive results could not be obtained because of hydrolysis of the element.

As the above results show, the trivalent species and pentavalent species must be separated immediately after the collection of the water samples.

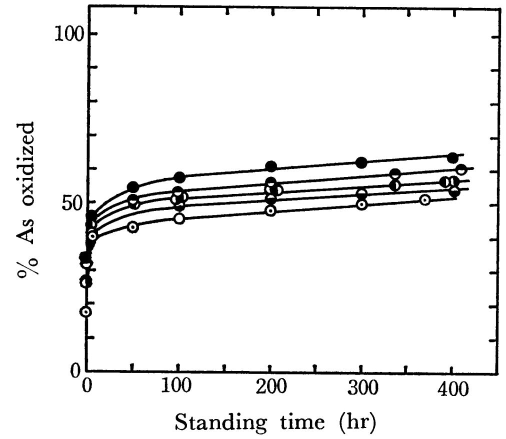

Fig. 1. Oxidation of arsenic(III) on standing in various salt solutions.
Without aeration; ⊙: 0.1 M NaClO$_4$, ◑: 0.025 M Na$_2$SO$_4$, ◐: 0.1 M NaCl
With aeration; ◒: 0.1 M NaClO$_4$, ◓: 0.025 M Na$_2$SO$_4$, ●: 0.1 M NaCl.

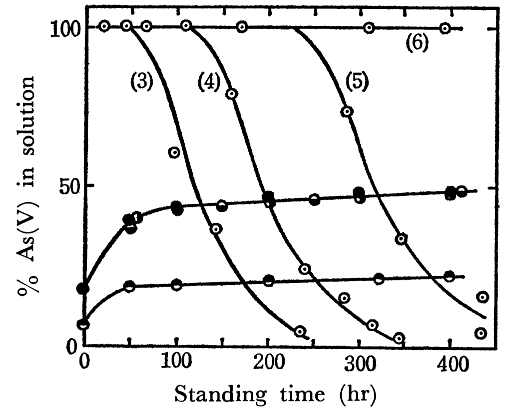

Fig. 2. Redox behavior of arsenic in sea water and artificial sea water.
●: sea water, As(III)→As(V), with aeration
◑: artificial sea water, As(III)→As(V), with aeration
◒: artificial sea water, As(III)→As(V), without aeration
◓: sea water, As(III)→As(V), without aeration
Curve (3): sea water, As(V)→As(III), without aeration, at 25 °C
Curve (4): sea water, As(V)→As(III), without aeration, at 10 °C
Curve (5): sea water, As(V)→As(III), with aeration, at 10 °C
Curve (6): sea water As(V)→As(III), with aeration, at 25 °C

Extraction Conditions for Arsenic and Antimony Diethyldithiocarbamates. The extraction conditions for arsenic and antimony diethyldithiocarbamates were studied, and following results were obtained.

1) Effect of pH Value: The effect of pH was investigated, using 1 ml of 1% Na-DDTC solution per 20 ml of sea water. Figure 3 shows that the optimum pH region is 2.5—5.0 for the separation of the trivalent species from the pentavalent species. Because the pH value shifts to a higher value during the extraction, the initial pH must be controlled in the range between 2.5 and 4.0.

Table 1. Arsenic and antimony concentrations in sea water

Sampling date and station	Sample No.	Depth m	As(III) μg/l	As(V) μg/l	Particulate μg/l	Total μg/l
Shirahama, Wakayama Pref. 30 Oct. 1970	1	0	0.22	1.49	0.02	1.73
	2	0	0.35	1.41	0.02	1.78
	3	0	0.17	1.38	0.01	1.56
Uragami, Wakayama Pref. 4 Nov. 1971	4[a]	0	0.14	1.56	0.04	1.74
	5[a]	0	0.14	1.44	0.08	1.66
	6[a]	0	0.15	1.24	0.04	1.43
	7[b]	0	0.22	1.45		1.67
	8[b]	40	0.36	1.50		1.86
Kojima, Osaka Pref. 1 Dec. 1970	9	0	0.22	2.20	0.03	2.45
	10	0	0.16	2.20	0.03	2.39
	11	0	0.17	1.66	0.01	1.84
	12	0	0.28	2.07	0.01	2.36

Sampling date and station	Sample No.	Depth m	Sb(III) μg/l	Sb(V) μg/l	Particulate μg/l	Total μg/l
Shirahama, Wakayama Pref. 30 Oct. 1970	1	0	0.06	0.38	0.01	0.45
	2	0	0.09	0.35	0.01	0.45
	3	0	0.05	0.31	0.01	0.37
Uragami, Wakayama Pref. 4 Nov. 1971	4[a]	0	0.03	0.19	0.02	0.24
	5[a]	0	0.03	0.16	0.02	0.21
	6[a]	0	0.06	0.12	0.02	0.20
	7[b]	0	0.03	0.13		0.16
	8[b]	40	0.05	0.18		0.23
Kojima, Osaka Pref. 1 Dec. 1970	9	0	0.06	0.41	0.02	0.49
	10	0	0.03	0.44	0.02	0.49
	11	0	0.10	0.47	0.03	0.60
	12	0	0.05	0.49	0.03	0.57

a) The Bay of Uragami. b) Outside the Bay.

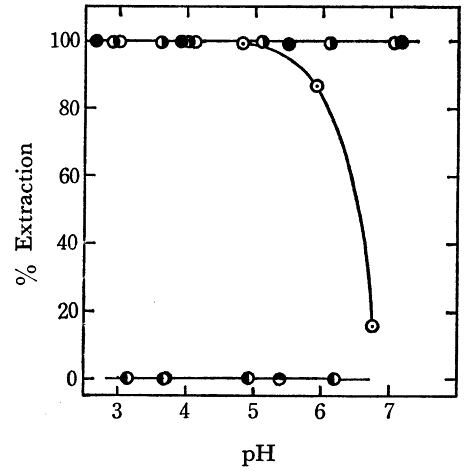

Fig. 3. Effect of pH on the extraction of arsenic and antimony diethyldithiocarbamates.
⊙: ^{74}As(III), ●: ^{122}Sb(III), ◑: Cu(II), ◐: ^{74}As(V) ◓: ^{124}Sb(V)

2) *Effect of Na–DDTC Concentration*: The effect of the amount of Na–DDTC was also studied by adding various amount of the reagent to 1 l of sea water containing the tracers and 2 μg of the carriers. More than 99% of the trivalent species could be extracted by adding 0.1 g or more of Na–DDTC per 1 l, and therefore, in subsequent experiments, 0.3 g of Na–DDTC was employed per 1 l of sea water.

3) *Effect of Nitric Acid Concentration on Back Extraction*: The back extraction of trivalent arsenic and antimony was effected by shaking the organic phase with an equal volume of nitric acid. As shown in Fig. 4, trivalent arsenic and antimony could be readily stripped into 3 M nitric acid. Sulfuric and hydrochloric acids were less effective.

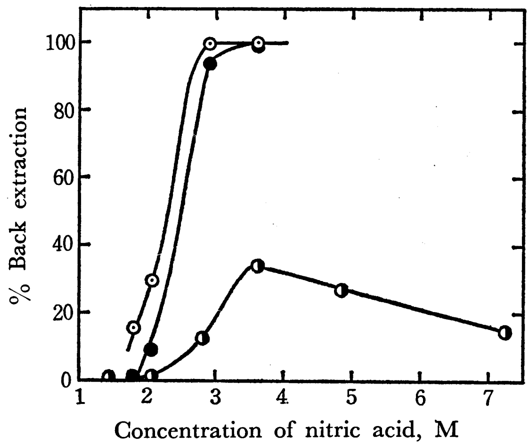

Fig. 4. Back extraction curves of arsenic(III), antimony(III), and copper(II).
⊙: As(III), ●: Sb(III), ◑: Cu(II).

In the practical procedure, 250 ml of chloroform was used for the extraction from 1 l of sea water sample, and at least 50 ml of 3 M nitric acid was needed for the back extraction. The more than 98.8% recovery could be attained.

Under these extracting and stripping conditions, copper, which is cocrystallized with thionalide, was quantitatively extracted, but incompletely stripped (see Fig. 4).

Table 2. Results of arsenic and antimony determinations on spiked samples

Sea water sample taken (litter)	As and Sb added (μg)	As(III) found (μg)	As(V) found (μg)	Sb(III) found (μg)	Sb(V) found (μg)
1	0	0.22[a]	1.49[a]	0.06[a]	0.38[a]
1	As(III) 0.5 + As(V) 1.0 + Sb(III) 0.5 + Sb(V) 0.5	0.74 (0.24)	2.51 (1.51)	0.55 (0.05)	0.90 (0.40)
1	As(III) 0.5 + Sb(III) 0.3	0.76 (0.26)	1.53	0.39 (0.09)	0.35
1	As(V) 1.0 + Sb(V) 0.5	0.20	2.45 (1.45)	0.08	0.85 (0.35)

a) The values are the amounts of the elements in the original samples of sea water (μg/l). The values in brackets are differences between the value in original sample of sea water and the analytical value.

4*) Effect of the Amount of Thionalide*: In previous research, arsenic and antimony could be quantitatively cocrystallized with thionalide from diluted sulfuric acid solution.[6] Since nitric acid was used for the back extraction of the trivalent arsenic and antimony, in the present experiments, the thionalide was cocrystallized from diluted nitric acid solution. Recovery of more than 98% was attained by adding 8 ml or more of 2% thionalide acetone solution to 1 l of 0.03—0.2 M nitric acid solution.

Analysis of As(III), As(V), Sb(III), and Sb(V) in Sea Water. The above procedure was recommended and applied to the determination of arsenic(III), arsenic(V), antimony(III), and antimony(V) in sea water samples. Surface sea water samples were collected from 5 stations, offshore from Shirahama and Uragami, Wakayama Prefecture, and from Kojima, Osaka Prefecture.

The analytical results are shown in Table 1. As shown in Table 1, the total contents of arsenic and antimony were in the range of 1.43—2.45 μg As/l and 0.16—0.60 μg Sb/l, and these values were in good agreement with the values found in previous studies[6] and with the data recently reported,[4,7,8–11] From 80 to 93% of the dissolved arsenic and from 74 to 94% of the dissolved antimony existed as arsenate and antimonate. This result also agrees with the results of Sugawara *et al.*[4,7] The result for antimony cannot be compared with others, because no report has been published on the valence state. Overall recovery in the pre- and post-irradiation procedure was over 98%.

In order to examine the accuracy of the proposed procedure for the determination of arsenic (III), (V) and antimony(III), (V), definite amounts of arsenic (III), (V) and antimony(III), (V) ions were added to sea water samples and the entire procedure for the determination of these elements was applied to the samples. The results of this spiking analysis are shown in Table 2. From these results, the relative error for the trivalent and pentavalent species of these elements was estimated to be less than ±10 percent and ±5 percent respectively. In this case, the concentrations of trivalent species were about one tenth of the concentrations of pentavalent species, and the analytical result for the former includes a comparatively large relative error. The blank value for arsenic was 0.01—0.03 μg and for antimony 0.005—0.01 μg.

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