BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1704—1708(1972)

Activation Analysis of Arsenic, Copper, and Antimony in Sea Water

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(Received September 16, 1971)

Arsenic, copper, and antimony in sea water were determined by the thermal neutron activation analysis. Convenient pre- and post-irradiation procedures were proposed and some samples were analyzed. Arsenic, copper, and antimony were collected by the cocrystallization with thionalide, and were irradiated for 30 min in the neutron flux of 2×10^{13} n/cm^2/sec. After the thionalide complex was decomposed with nitric acid, the copper and antimony were separated from the arsenic by precipitating with oxine, and the arsenic in the filtrate was coprecipitated with ferric hydroxide. Gamma-ray spectra were obtained and the decays of the 0.44—0.67 MeV photo peak of ^{64}Cu plus ^{122}Sb and the 0.55 MeV peak of ^{76}As were followed. The arsenic, copper, and antimony contents in sea water were estimated to be 1.12—1.71 μg As/*l*, 1.49—3.35 μg Cu/*l*, and 0.22—0.57 μg Sb/*l*.

Many workers have studied on the amount of arsenic and copper in sea water. Gorgy *et al.*,[1] Rakestraw and Lutz.[2] and Ishibashi *et al.*[3] determined the total amount of arsenic in sea water by the arsenomolybdate blue method or Gutzeit method, and found 15—35 μg As/*l*, 6—28 μg As/*l*, and 3—6 μg As/*l*, respectively. However, these methods give generally high values, that may result from arsenic impurity contained in the zinc and the acid employed, which sometimes exceeds the amount of arsenic in sea water. Smales and Pate[4,5] stated that the activation analysis could minimize the errors caused by the contamination from the reagents, and they found 1.6—5 μg As/*l* in sea water. Portmann and Riley[6] also gave the value of 2 μg As/*l* in sea water spectrophotometrically by molybdenum blue method, after concentrating arsenic by the thionalide cocrystallization.

The copper content in sea water have been reported to be in the range 1—20 μg Cu/*l*. Riley[7] searched for the favorable method for the determination of copper in such a low concentration, and pointed out that much of the earlier works were unreliable because of the poor analytical technique and the contamination. Brooks *et al.*[8] applied the atomic absorption spectrophotometry, and found 0.7—1.5 μg Cu/*l* in sea water; the value was in good agreement with Riley and Shinhaseni's data.[9] On the antimony content in sea

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[1] S. Gorgy, D. L. Fox, and N. W. Rakestraw, *J. Marine Res.*, **7**, 22 (1948).

[2] N. W. Rakestraw and F. B. Lutz, *Woods Hole Biol. Bull.*, **65**, 397 (1933).

[3] M. Ishibashi, T. Shigematsu, Y. Nishikawa, and Y. Ishibashi, *Record Oceanog. Works Japan*, **5**, 66 (1960).

[4] A. A. Smales and B. D. Pate, *Anal. Chem.*, **24**, 717 (1952).

[5] A. A. Smales and B. D. Pate, *Analyst*, **77**, 188 (1952).

[6] J. E. Portmann and J. P. Riley, *Anal. Chim. Acta*, **31**, 509 (1964).

[7] J. P. Riley and G. Skirrow, "Chemical Oceanography," Vol. 2, Academic Press, London and New York, (1965), p. 295.

[8] R. R. Brooks, B. J. Presley, and I. R. Kaplan, *Anal. Chim. Acta*, **38**, 321 (1967).

[9] J. P. Riley and P. Shinhaseni, *Analyst*, **83**, 299 (1958).

water, a few reports[10—12] have been published. Portmann[10] analyzed the Irish sea water samples spectrophotometrically and estimated to be 0.13—0.40 μg Sb/*l*.

Since the concentration of arsenic, copper, and antimony in sea water are very low, as described above, a suitable concentrating technique and sensitive analytical method have been desired. The neutron activation coupled with the thionalide cocrystallization seems to be one of the most attractive techniques, because of the simple and rapid procedure, the high sensitivity, and the minimum contamination. But ^{64}Cu, ^{76}As, and ^{122}Sb, which are available radioactive nuclides for the analysis, show the gamma photo peaks in the similar energy region. Moreover, the half-lives of ^{64}Cu (12.8 h) and ^{76}As (26.5 h) are too close to be used in the decay curve analysis. In this research, a simple and convenient chemical procedure for the neutron activation analysis of arsenic, copper, and antimony in sea water was recommended. These elements were concentrated by means of the thionalide cocrystallization, and after the neutron irradiation, copper and antimony were precipitated with oxine, arsenic was coprecipitated with ferric hydroxide, and the ^{76}As, ^{64}Cu, and ^{122}Sb activities were measured by the gamma-ray spectrometry. Some sea water samples were analyzed by this method, and furthermore, to search on the dissolved form of these elements, the particle size distribution of the elements was also investigated.

Experimental

Materials. Thionalide solution, 2% (w/v); 2 g of thionalide (Thioglycollic-β-aminonaphthalide) was dissolved in acetone and diluted to 100 m*l* with acetone. The solution was freshly prepared as required.

Sulfuric acid, 6N; Arsenic-free sulfuric acid was diluted with water.

Standard solution of arsenic, 10 μg/m*l*; 0.1607 g of arsenic trioxide was dissolved in diluted sodium hydroxide solution, which was neutralized with diluted sulfuric acid and diluted to 100 m*l* with water. This stock solution (1 mg As per m*l*) was diluted to make a working standard solution containing 10 μg of arsenic per m*l*.

Standard solution of antimony, 10 μg/m*l*; 0.2669g of potassium antimonyl tartrate ($K[Sb(C_4H_2O_6)(H_2O)]$) was dissolved in sulfuric acid and diluted to 100 m*l* with 6N sulfuric acid. This stock solution (1 mg Sb per m*l*) was diluted with 6N sulfuric acid to make a standard solution containing 10 μg of antimony per m*l*.

Standard solution of copper, 10 μg/m*l*; 0.3929 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) was dissolved in water, and after 5 m*l* of 6N sulfuric acid was added, diluted to 100 m*l* with water. The stock solution was diluted to get a solution containing 10 μg of copper per m*l*.

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

All the other reagents were the reagent grade, and employed without the further purification. Redistilled water was used in all the procedures.

Apparatus. Gamma-ray spectra were obtained with a well-type 3″×3″ NaI(Tl) scintillation detector connected to a Hitachi Gammascope, Model RAH-403 (a 400 channel pulse height analyzer), and the radioactivity measurements in the tracer experiments were made with a 2″×2″ NaI(Tl) detector connected to a Hitachi scalor, Model RC-2.

Procedure. *Pre-irradiation*: Immediately after the sampling, 1 *l* of sea water was successively filtered through a 8 μ pore-size Millipore filter and a 0.45 μ pore-size Millipore filter. To the filtered sample was added 0.3 g of ascorbic acid, and the solution was heated just under the boiling point, for 30 min (to reduce arsenic(V) to arsenic(III)). After 5 m*l* of 6N sulfuric acid and 8 m*l* of 2% thionalide acetone solution were added to the cooled solution with vigorous stirring, and the solution was boiled for about 30 min and then allowed to stand overnight at room temperature. The precipitate was filtered with a Millipore filter (pore size; 0.45 μ) and washed with water.

Irradiation: Two Millipore filters employed for the filtration of sea water sample and the filter including the thionalide precipitate were separately packed in three polyethylene capsule (8 mm long × 12 mm in diameter), which were stuffed in a polyethylene rabbit tube. The sample and the standard material were irradiated for 30 minutes in a neutron flux of 2×10^{13} n/cm^2·sec in KUR.

Post-irradiation: After cooling a few hours, the irradiated sample was treated with 20 m*l* of nitric acid containing 5 mg of copper, 1 mg of arsenic, and 0.3 mg of antimony carriers, and was decomposed by fuming to almost dryness. The residue was dissolved with 3 m*l* of 1N nitric acid, and copper and antimony were precipitated as the oxinates by adding 5 m*l* of 2% oxine solution at pH 7—8. Arsenic remaining in the filtrate was coprecipitated with ferric hydroxide at pH 8 by adding 10 mg of ferric ion, after the excess oxine was removed as the copper chelate (10 mg of copper was added).

Radioactivity Measurement: The copper and antimony oxinates and the ferric hydroxide precipitates were used for the gamma ray spectrometry of ^{64}Cu, ^{122}Sb, and ^{76}As. For the hydroxide precipitate, the 0.55 MeV photo peak of the gamma rays following to the decay of ^{76}As was measured. For the oxinates precipitate, the decay of the photo peak area from 0.44 to 0.67 MeV, which was the sum of the 0.51 MeV annihilation gamma rays of ^{64}Cu and the 0.57 MeV gamma rays of ^{122}Sb, was followed for one week.

Results

Thionalide Cocrystallization of Copper, Arsenic, and Antimony. In order to establish the pre-irradiation procedure, the conditions for the cocrystallization, such as the acidity of sulfuric acid and the amount of thionalide, were studied by using the radioactive tracers, ^{64}Cu, ^{76}As, and ^{124}Sb.

The tracer and 5 μg of the carrier were added to 1 *l* of sea water, and the recovery of the cocrystallization with thionalide was obtained by comparing the gamma activity with that of the original tracer solution.

1) Effect of Sulfuric Acid Concentration: The effect of sulfuric acid concentration on the recovery is shown in Fig. 1.

Copper(II), arsenic(III), and antimony(III), (V) are

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[10] J. E. Portmann and J. P. Riley, *Anal. Chim. Acta*, **35**, 35 (1966).

[11] I. Noddack and W. Noddack, *Ark. Zool.*, **1**, 32 (1940).

[12] D. F. Schutz and K. K. Turekian, *Geochim. Cosmochim. Acta*, **29**, 259 (1965).

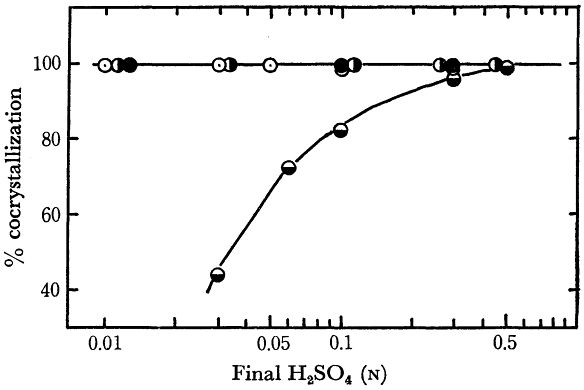

Fig. 1. Effect of sulfuric acid concentration on cocrystallization with thionalide (Thionalide: 160 mg/l of sea water).
⊙: As(III), ◒: As(V), ●: Sb(III), (V), ◑: Cu(II)

almost quantitatively recovered in the range from 0.01 N to 0.5 N sulfuric acid concentration, while the recovery of arsenic(V) is incomplete in this range, and reaches to a maximum value (about 97%) at 0.5 N sulfuric acid. The volume of sulfuric acid used must be as small as possible, for minimizing the contamination from the acid, and therefore, arsenic(V) is reduced to arsenic(III) with ascorbic acid, and the acidity is maintained at 0.03 N.

Table 1. Recovery of arsenic, copper and antimony using various volume of 2% thionalide

Volume of thionalide added (ml)	% Recovery		
	As	Cu	Sb
3	62.8		
5	95.8	96.2	94.8
7	98.3	98.3	98.6
8	98.6	98.9	98.6
10	99.4		99.3
12	99.8	99.2	99.5
15	99.8		

2) *Effect of the Amount of Thionalide on the Cocrystallization*: The effect of the thionalide amount was studied by adding the different amount of 2% thionalide solution to 1 l of sea water containing the tracer, 5 μg of the carrier and ascorbic acid, which was kept at 0.03 N with sulfuric acid. The results are presented in Table 1. The recovery of more than 98 per cent can be obtained by addition of 7 ml or more of 2% thionalide solution, and therefore, in the further experiments, 8 ml of 2% thionalide is employed per 1 l of sea water.

Chemical Separation with Oxine. Because ^{64}Cu and ^{76}As emit the gamma rays of the similar energies and have the half lives not so different from each other, neither the gamma ray spectrometry nor the decay curve analysis was successful to estimate the activity of each of the nuclides. The post-irradiation procedure, described above, was designed and preliminarily tested by the tracer experiments. The precipitate of oxinates was filtered with a glass filter, then dissolved into hydrochloric acid solution of a constant volume and the gamma activity of the solution was compared with that of the same volume of original tracer solution. The percentage of precipitation *vs.* pH curves are shown in Fig. 2.

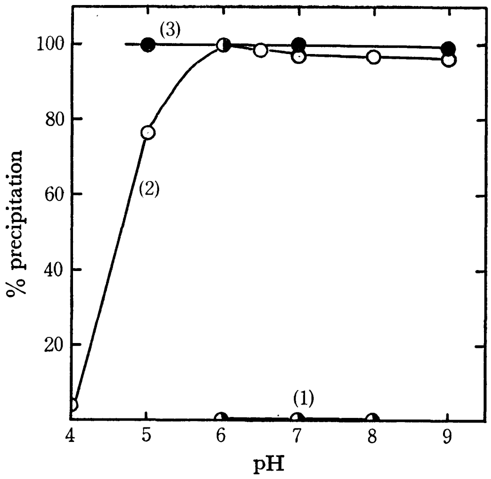

Fig. 2. Effect of pH on the precipitation of oxinates.
(1): As, (2): Sb-oxinate, (3): Cu-oxinate

Copper and antimony are almost quantitatively precipitated in the pH range from 6 to 9, but arsenic remains in the solution, which is readily recovered by coprecipitation with ferric hydroxide at a pH between 6 and 9. The overall recovery in the pre- and post-irradiation procedures is to be 98.6±3.5%.

Analysis of Sea Water Samples. Sea water samples were collected from 11 stations, 137—139° E and 31—34° N. At the station No. 5, six samples were obtained from the surface to a depth of 500 m. Samples at stations No. 9, No. 10, and No. 11 were used for the study of the adsorption of arsenic, copper, and antimony on the vessel wall in the storage.

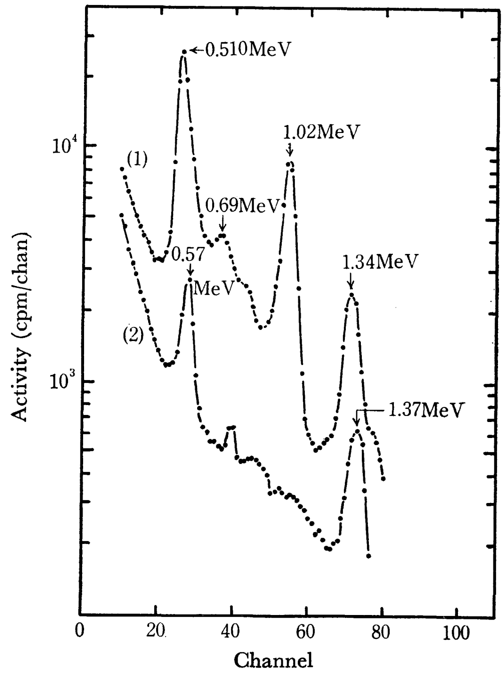

Fig. 3. Gamma-rays spectra of $^{64}Cu+^{122}Sb$ in sample (1): 10 h, (2): 125 h after irradiation.

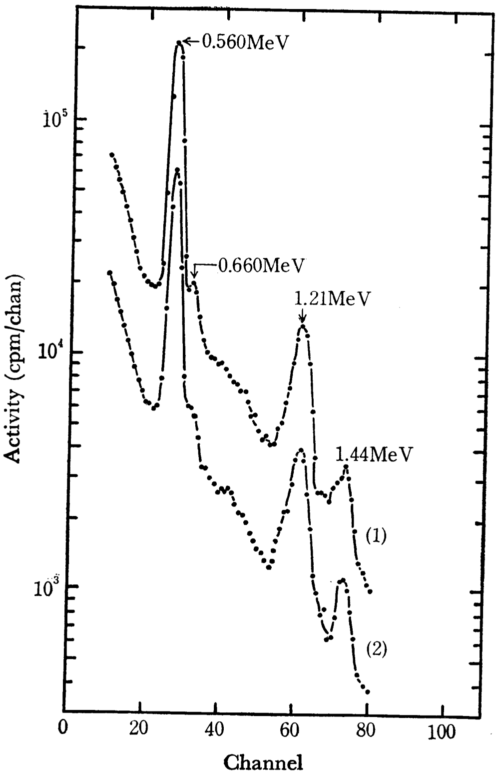

Fig. 4. Gamma-rays spectra of ^{76}As in sample (1): 10 h, (2): 25 h after irradiation.

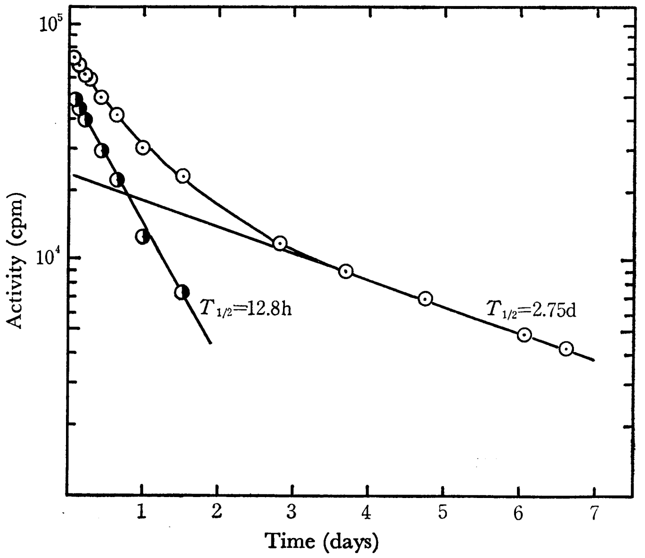

Fig. 5. Decay curves of ^{64}Cu($T_{1/2}$=12.8 h) and ^{122}Sb($T_{1/2}$= 2.75 d).

These samples were analyzed according to the procedure described above. The typical gamma ray spectra of the copper and antimony fraction and the arsenic fraction are shown in Figs. 3 and 4, and the decay curves are presented in Figs. 5 and 6 respectively.

By the present procedures, 0.01 μg of arsenic, copper and antimony could be detected. However, the results of the blank test were as follows; As: 0.01—0.03 μg, Cu: 0.02 μg, Sb: 0.007—0.01 μg. The analytical results are summarized in Table 2. The relative error of the duplicated analysis was estimated to be within ±5%.

Table 2. Analysis of arsenic, copper, and antimony in sea water

No.	Sampling date and station	Fraction	As (μg/l)	Sb (μg/l)	Cu (μg/l)
1	34°20.5′N	>8μ	0.09	<0.01	0.82
	138°00.5′E	0.45—8μ	0.01	<0.01	0.46
	22, Nov. 1969	Filtrate	1.40	0.44	0.22
	Surface	Total	1.50	0.44	1.50
2	33°40.8′N	>8μ	0.02	<0.01	0.97
	137°59.2′E	0.45—8μ	0.01	<0.01	0.69
	22, Nov. 1969	Filtrate	1.19	0.35	0.23
	Surface	Total	1.22	0.35	1.89
3	32°54.5′E	>8μ	<0.01	0.02	1.07
	138°01.5′E	0.45—8μ	<0.01	0.01	0.65
	23, Nov. 1969	Filtrate	1.28	0.27	0.46
	Surface	Total	1.28	0.30	2.18
4	32°21.0′N	>8μ	<0.01	0.01	0.42
	137°59.0′E	0.45—8μ	<0.01	0.01	0.89
	24, Nov. 1969	Filtrate	1.21	0.24	2.01
	Surface	Total	1.21	0.26	3.32
5-1	31°38.5′N	>8μ	0.20	0.04	0.55
	138°02.0′E	0.45—8μ	0.03	0.01	0.33
	24, Nov. 1969	Filtrate	1.35	0.26	0.67
	Surface	Total	1.58	0.31	1.55
5-2	31°38.5′N	>8μ	0.35	0.03	0.58
	138°02.2′E	0.45—8μ	0.02	0.07	0.24
	24, Nov. 1969	Filtrate	0.79	0.32	0.82
	Depth: 20m	Total	1.16	0.42	1.64
5-3	31°38.5′N	>8μ	0.04	0.04	0.26
	138°02.0′E	0.45—8μ	0.03	0.02	0.22
	24, Nov. 1969	Filtrate	1.17	0.20	0.61
	Depth: 100m	Total	1.24	0.26	1.06
5-4	31°38.5′N	>8μ	0.03	0.03	0.10
	138°02.0′E	0.45—8μ	0.03	0.02	0.16
	24, Nov. 1969	Filtrate	1.28	0.17	0.83
	Depth: 300m	Total	1.34	0.22	1.09
5-5	31°38.5′N	>8μ	0.05	0.03	0.18
	138°02.0′E	0.45—8μ	0.06	0.05	0.28
	24, Nov. 1969	Filtrate	1.59	0.22	0.76
	Depth: 500m	Total	1.70	0.30	1.22
6	32°15.0′N	>8μ	0.08	0.01	0.92
	139°13.0′E	0.45—8μ	0.01	0.01	0.49
	24, Nov. 1969	Filtrate	1.03	0.32	0.43
	Surface	Total	1.12	0.33	1.84
7	33°00.0′N	>8μ	<0.01	0.02	0.88
	139°56.5′E	0.45—8μ	<0.01	0.02	0.42
	25, Nov. 1969	Filtrate	1.40	0.39	0.35
	Surface	Total	1.40	0.43	1.65
8	34°29.9′N	>8μ	<0.01	0.04	0.94
	138°59.2′E	0.45—8μ	<0.01	0.04	0.41
	26, Nov. 1969	Filtrate	1.30	0.15	0.71
	Surface	Total	1.30	0.23	2.06

Discussion

The total contents of these elements in sea water are in the range of 1.12—1.71 μg As/l, 1.49—3.35 μg Cu/l, and 0.22—0.57 μg Sb/l. The concentration of arsenic well agrees with the value of Portmann and Riley,[6] and the content of antimony also agrees with

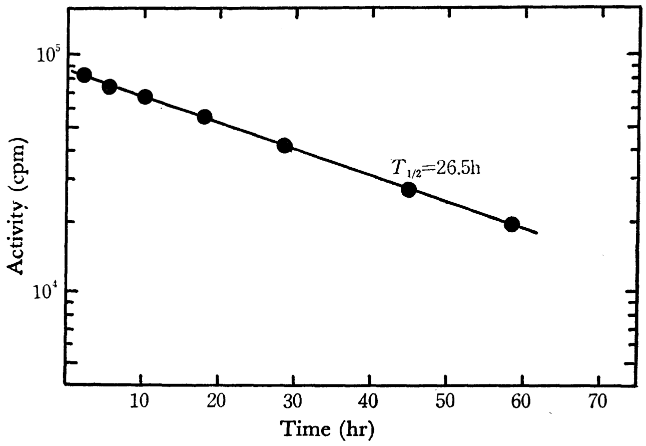

Fig. 6. Decay curve of ^{76}As($T_{1/2}$=26.5 h).

those of Noddack and Noddack,[11] Schutz and Turekian,[12] and Portmann and Riley.[10] The amount of copper is in the good agreement with the results of Fabricand *et al.*,[13] Riley and Shinhaseni.[9] and Brooks *et al.*[8]

The particle-size distribution suggests that the most parts of arsenic and antimony occur in soluble ionic state, passing through the 0.45 μ pore-size filter. 70—80% of copper exists in the particle species (about 50% distribution in the particles of larger than 8 μ, and 20—30%, in the particles of 0.45—8 μ), except for samples at station No. 4 and No. 5, in which about a half part of copper exists in the soluble ionic state. This phenomenon might be caused by the fact that the stations No. 4 and No. 5 were influenced by the Kuroshio Stream.

The vertical distributions of these elements were obtained at the station No.5. The total content and the particle size distribution slightly varried from the surface to 100 m depth, but in more than 100 m depth, they seemed to be almost changeless. After sample No. 9 was stored for 80 days, arsenic, copper, and antimony remaining in the solution and adsorbed on to the vessel wall were separately determined. For sample No. 10 and No. 11, the sample water was filtered with a 0.65 μ pore-size Millipore filter after the 30 days storage, and the analysis was made on the filtrate, the Millipore filter and the vessel wall. The results are shown in Table 3, from which it was deduced that the samples should be analyzed within a few days after the sampling.

Table 3. % Adsorption onto vessel wall in storage of sea water

No.	Sampling date and station	Fraction	% distribution		
			As	Cu	Sb
9	33°58.5′N	Adsorpt.	5.31	40.66	17.65
	137°31.5′E		(0.07)	(1.24)	(0.09)
	31, July, 1969	Soln.	94.69	59.34	82.35
	Surface		(1.25)	(1.81)	(0.42)
10	33°29.0′N	Adsorpt.	5.06	25.77	10.86
	136°02.0′E		(0.07)	(0.84)	(0.05)
	10, Oct. 1969	>0.65μ	7.25	36.50	8.71
	Surface		(0.10)	(1.19)	(0.04)
		Filtrate	87.68	37.73	80.43
			(1.21)	(1.23)	(0.37)
11	33°29.5′N	Adsorpt.	5.67	33.22	8.51
	135°15.0′E		(0.08)	(1.01)	(0.04)
	10, Oct. 1969	>0.65μ	7.09	33.88	10.64
	Surface		(0.10)	(1.03)	(0.05)
		Filtrate	87.23	32.90	80.85
			(1.23)	(1.00)	(0.38)

No. 9: 80 days storage, No. 10, No. 11: 30 days storage.
The values in bracket were expressed the amount of the elements; (μg/*l*).

The author wishes to express his sincere thanks to Professor Tsunenobu Shigematsu, Institute for Chimical Research, Kyoto University, and Professor Yasuharu Nishikawa, Faculty of Science and Technology, Kinki University, for their kind advice and suggestion throughout this work. The author is deeply indebted to Hot Laboratory groups of Kyoto University for their helps in the irradiation operation, and also indebted to Professor Shiro Okabe, Faculty of Oceanography, Tokai University, for his kind help in the sampling of sea water.

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13) B. P. Fabricand, R. R. Sawyer, S. G. Ungar, and S. Adler, *Geochim. Cosmochim. Acta,* **26**, 1023 (1962).