

## The Contents and Distributions of Arsenic, Antimony, and Mercury in Geothermal Waters

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The contents and distributions of arsenic, antimony, and mercury in geothermal water samples taken from various geothermal areas in Japan were investigated. Since the existing forms of arsenic, antimony, and mercury in geothermal waters are complex and can change during sample storage, it is difficult to determine all of the chemical forms. In this study, therefore, the arsenic(III+V), antimony(III+V), and total mercury contents were determined. In geothermal water, there is a high positive correlation between the contents of arsenic and antimony. However, there is no correlation at all between the contents of mercury and arsenic, or between those of mercury and antimony. It can be assumed that mercury behaves differently from either arsenic or antimony in geothermal water.

In keeping pace with the development of geothermal energy, attention has been paid to the various components of geothermal water, such as that of thermal water or hot spring water. Arsenic, antimony and mercury are included in these components. However, information on the contents, existing forms and distributions of these elements are insufficient. Investigations concerning arsenic have been continuing in view of the environmental contamination caused by the drainage of hot spring water<sup>1)</sup> and the use of hot spring water for drinking.<sup>2,3)</sup> In some sources of thermal well water obtained for geothermal power generation, there are high concentrations of arsenic; such thermal water is being recharged into underground regions as a counterplan. Investigations into the exclusion treatment of arsenic have also begun.<sup>4)</sup>

Since antimony, the homologous element of arsenic, is found in relatively low content, compared to arsenic, and is difficult to analyze, there have not been many reports on antimony in geothermal water compared to those on arsenic. After Holak<sup>5)</sup> developed atomic absorption spectrometry for arsenic hydride in 1969, determinations of arsenic and antimony in ppb-ppt levels became possible through the work of Fernandez et al.<sup>6)</sup> and Yamamoto et al.<sup>7)</sup>

To determine the mercury content, cold vapor atomic absorption spectrometry has been widely employed.<sup>8,9)</sup>

Nakagawa<sup>10)</sup> and Awaya et al.<sup>11)</sup> produced data concerning the mercury content in hot spring water at various locations in Japan.

There have been many reports concerning the arsenic and antimony contents in hot spring water at various specific areas.<sup>12–18)</sup> There have also been reports by Watanuki et al.<sup>19)</sup> and Sato<sup>20)</sup> concerning the arsenic and antimony contents in acidic thermal water. However, there have been no reports concerning measurements of the contents of arsenic, antimony and mercury in the geothermal water found over a wide range of geothermal areas. In this study, we determined the contents of arsenic, antimony and mercury

in geothermal water (thermal water, hot spring water and condensed water) sampled at various geothermal areas in Japan. We discuss their existing forms, mutual relations and distributions.

### Experimental

**Preservation of Sample.** Geothermal water samples used for determining arsenic and antimony contents were kept in polyethylene bottles (1 l), which were exuded beforehand by approximately 3 mol dm<sup>-3</sup> nitric acid for two weeks and then washed thoroughly with water. 10 ml of 35% hydrochloric acid was added to each 1 l of sample at the sampling place as quickly as possible. Samples were then brought back to the laboratory and analyzed.

The samples used in determinations of the mercury content were taken in hard glass bottles, which had been washed in a manner similar to that of the polyethylene bottles used for arsenic and antimony, equipped with Teflon packing. For every 1 l of sample, 10 ml of (1:1) (97%) sulfuric acid was added. Samples were then brought back to the laboratory and analyzed. When a sample containing much chloride, such as geothermal water, was preserved at less than pH 1, the loss of mercury was hardly observable. However, for samples containing much sulfide, the loss of arsenic, antimony, and mercury could be observed. In this case, the sulfide and its related compounds were oxidized by a sulfuric acid-potassium permanganate solution and determinations of arsenic, antimony, and mercury were quickly undertaken.

The acids (hydrochloric acid, sulfuric acid) and the potassium permanganate, which were used for measurements of arsenic, antimony and mercury were all analytical, special-reagent grade.

The present investigation aimed to provide a practical method for determining the contents of arsenic and antimony. Regarding arsenic and antimony determination we used the method of Yamamoto et al.,<sup>7)</sup> and applied a differential determination of arsenic and antimony to geothermal waters. The procedures are as follows.

**Determination of Arsenic.** One method for a differential determination of arsenic(III+V) and arsenic(III) is described.

A sample solution ( $\leq 40$  ml), containing less than 0.5  $\mu\text{g}$  of arsenic(III+V), was placed in a reaction vessel and diluted with water, bringing it to 40 ml. Into this solution, 10 ml of

a) Ebino rotenburo. b) Iwōdani miyōban onsen. c) Ebino iwōyamashita (1). d) Kirishima kokusaihoteru. e) Ebino iwōyamashita (2). f) 10ml of 35% hydrochloric acid was added to each 1 liter of sample.

Table 2. Analytical Results of Mercury in Various Geothermal Waters

Sampling station	Inorg. Hg	Inorg. Hg+Org. Hg	Total Hg	Remarks
	ng l <sup>-1</sup>	ng l <sup>-1</sup>	ng l <sup>-1</sup>	
Unagionsen(Yamagawa)	3.7	6.3	6.3	Hot spring water
Miyōban(Iwōdani)	0.7	5.0	4.7	Hot spring water
Rotenburo(Ebino)	2.9	4.9	5.0	Hot spring water
Iwōyamashita(Ebino)	1.7	2.2	18.5	Hot spring water
Kankyō-chōsasei(Tearai)	2.9	3.2	10.5	Thermal water
Fushime(Yamagawa)	8.7	9.9	11.0	Thermal water
Ōtake(Ōita)	10.6	13.3	14.7	Thermal water
Matsukawa No. 6 (Matsukawa)	0.1	9910	13700	Condensed water
Matsukawa No. 7 (Matsukawa)	0.1	9020	11400	Condensed water
Kankyō-chōsasei(Tearai)	2.3	4640	4600	Condensed water

Table 3. Analytical Results of Arsenic, Antimony, and Mercury in Geothermal Waters

No.	Sampling location	Date	Temp	pH	As(III+V)	Sb(III+V)	Hg(Total)
			°C		μg l <sup>-1</sup>	μg l <sup>-1</sup>	ng l <sup>-1</sup>
1	Usu(Ginnumakakō)	Nov. 13. '82	90	3.0 <sub>6</sub>	1.7	0.0 <sub>5</sub>	89.8 <sup>a)</sup>
2	Tōya(Soubetsu onsen) (1)	Nov. 14. '82	59.7	6.5 <sub>9</sub>	910	0.3 <sub>8</sub>	10.8
3	Tōya(Soubetsu onsen) (2)	Nov. 14. '82	67.0	6.4 <sub>9</sub>	1160	0.2 <sub>5</sub>	10.2
4	Noboribetsu onsen	Oct. 25. '83	87.5	2.5 <sub>4</sub>	23.2	0.8 <sub>6</sub>	10.1
5	Osorezan (1)	Nov. 15. '82	58.0	2.1 <sub>6</sub>	16.0	0.2 <sub>0</sub>	7.5
6	Osorezan (2)	Nov. 15. '82	59.6	2.0 <sub>5</sub>	1.4	0.0 <sub>5</sub>	37.0
7	Osorezan (3)	Nov. 15. '82	62.6	2.0 <sub>2</sub>	1430	0.1 <sub>5</sub>	30.8
8	Osorezan (4)	Nov. 15. '82	61.5	2.0 <sub>0</sub>	20.0	0.0 <sub>5</sub>	10.2
9	Tamagawa onsen Ōubuki	Sept. 8. '82	98.0	1.2 <sub>0</sub>	3050	7.8	22.6
10	Ōnuma (1)	Sept. 8. '82	—	7.9 <sub>1</sub>	9500	163	18.7
11	Ōnuma (2)	Sept. 8. '82	—	7.8 <sub>2</sub>	8050	153	19.1
12	Kuroyu	Sept. 9. '82	86.0	2.9 <sub>9</sub>	0.3 <sub>5</sub>	0.0 <sub>8</sub>	—
13	Doroyu	Sept. 10. '82	97.2	8.1 <sub>3</sub>	7.0	0.7 <sub>5</sub>	—
14	Oyasukyō Ōubukiyu	Sept. 10. '82	—	8.3 <sub>8</sub>	160	14.7	26.5
15	Dowa kōgyō(Sumikawa)	Sept. 10. '82	93.5	9.3 <sub>8</sub>	211	22.6	21.1
16	Kakkonda (1)	Oct. 30. '81	—	8.3 <sub>5</sub>	3350	146	43.0
17	Kakkonda (2)	Oct. 30. '81	87.5	8.6 <sub>0</sub>	2610	119	16.6
18	Kakkonda (3)	Oct. 15. '82	—	8.4 <sub>4</sub>	4500	147	13.6
19	Kakkonda (4)	Oct. 15. '82	—	8.7 <sub>8</sub>	2100	111	15.2
20	Kakkonda(Damushita onsen)	Oct. 30. '81	98.1	8.8 <sub>3</sub>	435	26.7	—
21	Onikoube (1)	Jun. 19. '82	93.0	4.7 <sub>0</sub>	1310	17.2	21.3
22	Onikoube (2)	Jun. 19. '82	97.3	7.1 <sub>8</sub>	1610	55.2	19.0
23	Onikoube (3)	Jun. 19. '82	97.4	3.4 <sub>6</sub>	1540	26.2	14.8
24	Onikoube Arayu	Jun. 19. '82	91.0	1.9 <sub>9</sub>	215	0.5 <sub>1</sub>	—
25	Katayamajigoku	Jun. 19. '82	92.1	2.5 <sub>0</sub>	8.6	1.4 <sub>7</sub>	—
26	Hakone(Ōwakudani)	Jul. 15. '83	—	2.3 <sub>9</sub>	1.8 <sub>6</sub>	0.0 <sub>4</sub>	65.5
27	Hakone(Miyanoshita-jakotsu)	Jul. 15. '83	86.0	8.0 <sub>6</sub>	1150	9.6 <sub>6</sub>	12.7
28	Sujiyu(Utaseyu)	Aug. 5. '83	55.3	3.4 <sub>9</sub>	306	5.1 <sub>0</sub>	19.2
29	Sujiyu(Yakushiyu)	Aug. 5. '83	55.0	3.5 <sub>1</sub>	330	5.9 <sub>0</sub>	4.5
30	Sujiyu(Oyu)	Aug. 5. '83	44.0	3.8 <sub>7</sub>	288	5.9 <sub>0</sub>	6.3
31	Hattyoubaru (1)	Aug. 5. '83	97.0	7.3 <sub>0</sub>	3660	119	6.8
32	Hattyoubaru (2)	Aug. 5. '83	96.5	7.1 <sub>7</sub>	4290	244	31.6
33	Hattyoubaru (3)	Aug. 5. '83	92.0	7.4 <sub>5</sub>	3670	70.5	4.6
34	Mizuwaketōge	Aug. 6. '83	96.2	8.9 <sub>8</sub>	480	21.8	2.6
35	Takigami	Aug. 3. '83	—	9.0 <sub>8</sub>	332	13.6	—
36	Otake	Nov. 9. '81	90	8.3 <sub>3</sub>	2590	88.8	14.7
37	Ebino rotenburo	Nov. 1. '81	40.5	2.2 <sub>3</sub>	15.4	0.1 <sub>5</sub>	9.7
38	Ebino rotenburo	Mar. 14. '82	39.0	2.2 <sub>5</sub>	41.5	0.7 <sub>0</sub>	5.0
39	Ebino rotenburo	Sept. 12. '82	40.5	2.3 <sub>1</sub>	10.4	0.1 <sub>5</sub>	11.7
40	Ebino rotenburo	Aug. 26. '83	39.5	2.3 <sub>5</sub>	12.4	0.3 <sub>4</sub>	13.5
41	Ebino rotenburo	Nov. 25. '83	37.5	2.3 <sub>9</sub>	7.3	0.2 <sub>0</sub>	7.1
42	Ebino iwōyamashita	Nov. 1. '81	56.0	1.8 <sub>5</sub>	60.5	0.9 <sub>7</sub>	12.2
43	Ebino iwōyamashita	Jan. 27. '82	45.8	1.8 <sub>5</sub>	47.3	1.0 <sub>3</sub>	9.8
44	Ebino iwōyamashita	Mar. 14. '82	49.0	1.7 <sub>0</sub>	45.7	1.4 <sub>2</sub>	9.2
45	Ebino iwōyamashita	Sept. 12. '82	58.5	1.8 <sub>4</sub>	60.8	0.9 <sub>3</sub>	9.4
46	Ebino iwōyamashita	Aug. 26. '83	57.8	1.8 <sub>8</sub>	73.7	1.0 <sub>1</sub>	9.7
47	Ebino iwōyamashita	Nov. 25. '83	46.0	1.9 <sub>7</sub>	75.6	0.8 <sub>0</sub>	6.8

Table 3. (Continued)

No.	Sampling location	Date	Temp	pH	As(III+V)	Sb(III+V)	Hg(Total)
			°C		$\mu\text{g l}^{-1}$	$\mu\text{g l}^{-1}$	$\text{ng l}^{-1}$
48	Iwōdani miyouban	Jan. 27. '82	58.3	3.0 <sub>0</sub>	86. <sub>3</sub>	0.0 <sub>8</sub>	8.5
49	Iwōdani miyouban	Mar. 13. '82	58.5	3.1 <sub>2</sub>	88. <sub>2</sub>	0.4 <sub>5</sub>	4.7
50	Iwōdani miyouban	Sept. 12. '82	60.0	3.1 <sub>5</sub>	225	0.1 <sub>3</sub>	3.6
51	Iwōdani miyouban(Iwōsen)	Aug. 26. '83	45.8	3.3 <sub>3</sub>	77. <sub>7</sub>	0.3 <sub>8</sub>	10. <sub>8</sub>
52	Iwōdani miyouban(Iwōsen)	Nov. 25. '83	50.7	3.3 <sub>0</sub>	43. <sub>2</sub>	0.0 <sub>8</sub>	3.4
53	Iwōdani miyouban(Tetsusen)	Aug. 26. '83	61.6	3.1 <sub>6</sub>	154	0.4 <sub>1</sub>	8.4
54	Iwōdani miyouban(Tetsusen)	Nov. 25. '83	61.3	3.1 <sub>8</sub>	104	0.1 <sub>3</sub>	9.6
55	Maruo 3 gōsen	Dec. 6. '81	76.0	6.4 <sub>5</sub>	3.8	0.1 <sub>8</sub>	7.7
56	Maruo 3 gōsen	Jan. 27. '82	77.2	6.5 <sub>8</sub>	1.7	0.0 <sub>5</sub>	54. <sub>6</sub>
57	Maruo 3 gōsen	Mar. 13. '82	73.8	6.9 <sub>1</sub>	2.3	0.0 <sub>8</sub>	72. <sub>5</sub>
58	Maruo 3 gōsen	Apr. 14. '82	75.5	6.7 <sub>1</sub>	2.0	0.1 <sub>5</sub>	51. <sub>7</sub>
59	Maruo 3 gōsen	Sept. 12. '82	76.8	7.7 <sub>0</sub>	1.3	0.1 <sub>0</sub>	61. <sub>3</sub>
60	Tearai (1)	Feb. 17. '82	92.5	8.6 <sub>8</sub>	4410	193	37. <sub>4</sub>
61	Tearai (2)	Feb. 25. '82	93.0	8.3 <sub>7</sub>	5800	205	65. <sub>5</sub>
62	Tearai (3)	Mar. 10. '82	94.0	8.1 <sub>7</sub>	7150	231	10. <sub>5</sub>
63	Tearai (4)	Oct. 6. '82	94.2	2.9 <sub>4</sub>	4450	92. <sub>3</sub>	8.4
64	Tearai (5)	Oct. 23. '82	96.5	2.7 <sub>2</sub>	5350	81. <sub>0</sub>	12. <sub>9</sub>
65	Kurino KEI-3	Jan. 27. '82	93.5	8.5 <sub>4</sub>	2650	145	21. <sub>7</sub>
66	Kurinodake onsen	Mar. 13. '82	64.1	1.9 <sub>5</sub>	1.7	0.1 <sub>5</sub>	17. <sub>0</sub>
67	Sunaburo(Ibusuki)	Jul. 9. '82	51.8	6.8 <sub>1</sub>	77. <sub>4</sub>	4.2 <sub>0</sub>	11. <sub>6</sub>
68	Shokubutsushikenjō(Ibusuki)	Jul. 9. '82	52.0	6.6 <sub>2</sub>	32. <sub>6</sub>	0.3 <sub>0</sub>	16. <sub>4</sub>
69	Nigatsuden(Ibusuki)	Jul. 9. '82	59.5	7.0 <sub>8</sub>	46. <sub>4</sub>	0.3 <sub>3</sub>	11. <sub>8</sub>
70	Hakusuikan(Ibusuki)	Jul. 9. '82	69.0	6.8 <sub>7</sub>	155	4.5 <sub>0</sub>	13. <sub>7</sub>
71	Kokuritsubyōin(Ibusuki)	Jul. 9. '82	78.0	7.8 <sub>0</sub>	62. <sub>4</sub>	3.6 <sub>0</sub>	11. <sub>7</sub>
72	Okachogamizu(Yamagawa)	Jul. 9. '82	52.5	7.0 <sub>6</sub>	74. <sub>0</sub>	1.8 <sub>3</sub>	9.8
73	Masuda onsen(Yamagawa)	Jul. 9. '82	76.0	8.0 <sub>8</sub>	109	7.5 <sub>8</sub>	3.8
74	Fushime(Yamagawa)	Jul. 9. '82	89.5	6.5 <sub>7</sub>	1540	73. <sub>6</sub>	27. <sub>9</sub>
75	Kaimonsou(Kaimon)	Jul. 9. '82	39.2	7.7 <sub>1</sub>	30. <sub>6</sub>	1.1 <sub>0</sub>	10. <sub>7</sub>
76	Matsukawa (1) <sup>b)</sup>	Oct. 28. '81	—	—	121	0.4 <sub>8</sub>	15900
77	Matsukawa (2) <sup>c)</sup>	Oct. 28. '81	—	—	97. <sub>3</sub>	0.5 <sub>3</sub>	13700
78	Matsukawa (3) <sup>d)</sup>	Oct. 28. '81	—	—	320	0.4 <sub>2</sub>	11400
79	Matsukawa (4) <sup>e)</sup>	Oct. 29. '81	—	—	114	0.3 <sub>5</sub>	—

a) Stored in a polyethylene bottle. b), c), d), e): Condensed water.

water. After sampling, the arsenic(III) and antimony(III) were exposed to an oxidative atmosphere and may have been converted to arsenic(V) and antimony(V), respectively.

Since arsenic(III) and antimony(III) in geothermal water can change, depending on the storage conditions of the sample, any determination of arsenic(III) and antimony(III) must be carried out in as short a time as possible after sampling.

#### Existing Forms of Mercury in Geothermal Waters.

The analytical results of the existing chemical forms are shown in Table 2.

In thermal water and hot spring water, there is no great difference in the contents of soluble inorganic mercury, soluble inorganic plus organic mercury, and total mercury. It may be noted that mercury in thermal water and hot spring water exists in almost soluble inorganic mercury. However, for volcanic gas condensed water, which contains much hydrogen sulfide, the amount of soluble inorganic plus organic mercury and the total amount of mercury is more than that of soluble inorganic mercury. This does not suggest that there is not much soluble inorganic mercury in volcanic gas condensed water, but implies that the

Table 4. Arsenic, Antimony, and Mercury Contents in Geothermal Waters

Element	Range <sup>a)</sup>	<i>n</i> <sup>b)</sup>	$\bar{X}_A$ <sup>c)</sup>	$\bar{X}_G$ <sup>d)</sup>
As	0.35—9500	75	1230	141
Sb	0.05—244	75	35. <sub>4</sub>	2.5 <sub>0</sub>
Hg	2.6 — 89. <sub>8</sub>	69	19. <sub>1</sub>	13. <sub>8</sub>

a—c) in  $\mu\text{g l}^{-1}$  for As, Sb and  $\text{ng l}^{-1}$  for Hg. b) Number of samples. c) Arithmetic mean. d) Geometric mean.

reduction of soluble inorganic mercury is difficult because of the interference of sulfide ion. Therefore, it is difficult to determine the amount of soluble inorganic mercury and organic mercury in geothermal water samples which contain much sulfide ion.

**The Arsenic, Antimony, and Mercury Contents in Geothermal Waters.** The arsenic(III+V), antimony(III+V), and total contents of mercury were determined for geothermal water sampled from various geothermal areas in Japan. The sampling stations are illustrated in Fig. 1 and analytical results are tabulated in Table 3. Below, we discuss the data listed in Table 3.

The range, arithmetic and geometric mean of the arsenic, antimony, and mercury contents and the

number of samples measured, except for gas condensed water, are shown in Table 4.

Using the mean content of arsenic, antimony, and mercury in igneous rocks, accepted to be 1.5,<sup>21)</sup> 0.2,<sup>22)</sup> and 0.08<sup>23)</sup> ppm, respectively, the gravimetric ratios of As/Sb, Sb/Hg, and As/Hg can be calculated as being 7.5, 2.5, and 19, respectively. From the values listed in Table 4, the gravimetric ratios of As/Sb, Sb/Hg, and As/Hg in geothermal water were calculated to be 56, 179 and 10000, respectively. Watanuki et al.<sup>19)</sup> have reported that the gravimetric ratio of As/Sb in the Tamagawa and Kusatsu hot springs to be 100 and 50, respectively.

The antimony and mercury contents in geothermal water are smaller compared to the arsenic content. The reasons involve (assuming the differences of the

composition of thermal water which comes into contact with igneous rock) the ease of sulfide precipitation and gas scattering in the atmosphere.

**Mutual Relation of Arsenic, Antimony, and Mercury in Geothermal Waters.** The mutual relation among arsenic, antimony and mercury contents in geothermal waters is shown in Figs. 2—4.

In geothermal water, there is a high positive correlation between the arsenic and antimony contents (correlation coefficient, 0.87). However, the correlation coefficients between the contents of arsenic and mercury or between that of antimony and mercury were 0.065 and 0.15, respectively, showing no correlation between arsenic and mercury or between antimony and mercury. This suggests that mercury behaves differently from arsenic and antimony in geothermal water.

**Distributions of Arsenic, Antimony, and Mercury in Geothermal Waters.** The frequency distributions of the arsenic, antimony, and mercury contents in geothermal water are shown in Figs. 5—7.

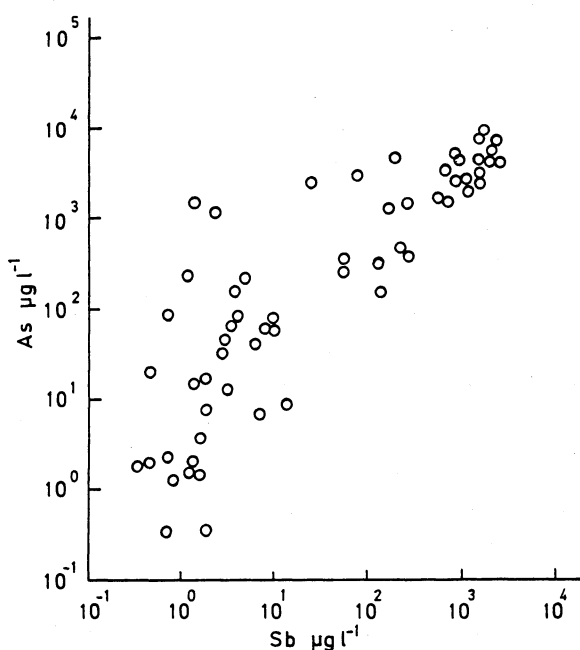


Fig. 2. Relation between arsenic and antimony in geothermal waters.

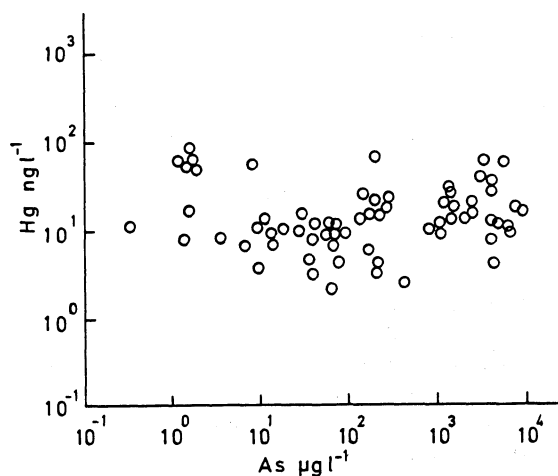


Fig. 3. Relation between mercury and arsenic in geothermal waters.

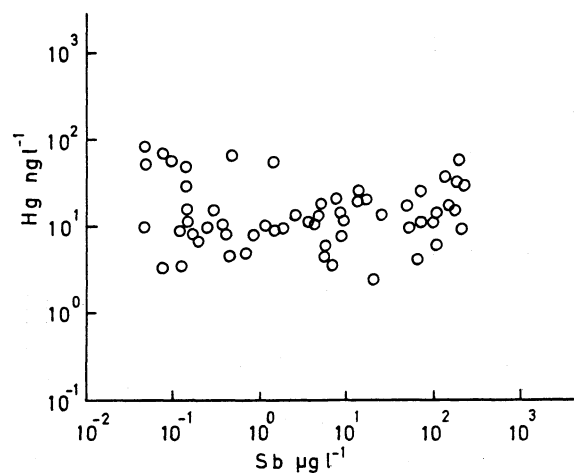


Fig. 4. Relation between mercury and antimony in geothermal waters.

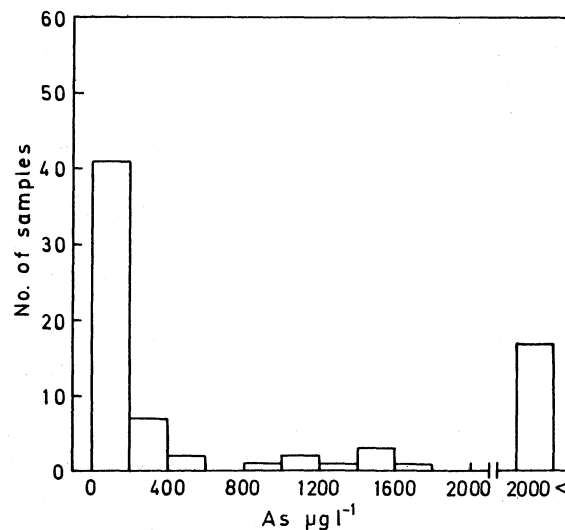


Fig. 5. Frequency for arsenic content distributions of geothermal waters.



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