BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1153—1154(1971)

The Mercury Content of Several Acid Hot Springs in Japan

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(Received October 24, 1970)

The geochemical data of mercury are still insufficiently especially for materials related to volcanic activity.[1] As to hot spring waters, two investigations have been reported hitherto. Stock and Cucuel[2] found 0.0001—0.0005g/ton mercury in spring water. Iwasaki *et al.*[3] reported on the chemical composition of Tamagawa Hot Spring, Akita Prefecture, in which the amount of mercury was estimated to be 0.01ppm. In this paper, the present authors will report the results of a quantitative estimation of mercury in several acid hot springs in Japan.

Sampling and Analytical Method

The samples shown in Table 1 were collected from 10 hot springs distributed around the Shirane volcano, Gunma Prefecture, on July 17th, 1970. The pH values and the temperatures were measured at the orifice of the springs. The determination of mercury was carried out in the laboratory according to the method of a previous work.[4] Mercuric sulfide should be

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2) A. Stock and F. Cucuel, *Naturwissenschaften,* **22,** 390 (1934).

3) I. Iwasaki, T. Katsura, T. Tarutani, T. Ozawa, M. Yoshida, B. Iwasaki, M. Hirayama, and M. Kamada, "Geochemistry of the Tamagawa Hot Springs," Dedicated to Prof. E. Minami by his friends and students on his sixtieth birthday, Published in Tokyo (1963), p.23; Y. Uzumasa, "Chemical Investigation of Hot Springs in Japan," Tsukiji Shokan Co., Ltd. (1965), p. 83.

4) N. Ohta, M. Terai, and M. Isokawa, *Nippon Kagaku Zasshi,* **91,** 351 (1970).

Table 1. Mercury content of acid hot springs

Sample	Temperature (°C)	pH	Hg ($\mu g/l$)
Yubatake, Kusatu	64.8	1.7	7.2
Gunma Univ. Hospital, Kusatu	56.5	1.7	19
Sainokawara No. 4, Kusatu	54.4	1.8	19
Sainokawara No. 6, Kusatu	45.8	1.8	30
Ubayu, Manza	81.0	2.3	<0.1
Ōnigayu, Manza	71.0	2.0	<0.1
Suzunoyu, Manza	96.5	2.0	<0.1
Karabuki, Manza	94.0	1.3	<0.1
Syakunage, Manza	90.0	1.8	<0.1
Yukama, Mt. Shirane	16.4	0.8	17

precipitated as quickly as possible after the sample has been collected in order to prevent any loss of mercury. Cadmium nitrate solution containing 2.5 mg of cadmium was added to 500 m*l* of sample water as a carrier. The acidity of the solution was adjusted to 0.1N. After the solution had then been saturated with hydrogen sulfide, 0.5 m*l* of 5% aluminum nitrate solution was added and the mixture was mixed well. After not less than 24 hr, the sulfide precipitate was filtered and treated with 3 m*l* of aqua regia. The solution was aerated for several minutes, and then 2 m*l* of 20% hydroxylamine hydrochloride solution were added. The pH of the solution was adjusted to 4.5 with ammonium hydroxide; the final volume should be approximately 50 m*l*. The cupric ion was eliminated from this solution by adding 5 m*l* of 0.1 mol/*l* trifluoroacetylacetone-chloroform solution and shaking it for 10 minutes. The aqueous solution was separated and adjusted to 0.25N in sulfuric acid. Five milliliters of 0.001% dithizone-chloroform solution were added to the solution, and the mixture was shaken for one minute. The chloroform phase was separated, and the absorbance was measured at 490 mμ with a Shimadzu-Bausch & Lomb Spectronic 20 spectrophotometer.

Results and Discussion

The mercury contents of the acid hot springs are shown in Table 1, together with the pH values and the temperatures. The average mercury contents of hot springs of the Kusatu and Manza districts are shown in Table 2, along with the previously-reported values of various natural waters.

The mercury content of spring water seems to differ much according to the locality and the type of each hot spring. The values of Kusatu and Yukama are high and close to the data reported by Iwasaki *et al.*[3] On the other hand, the values of Manza are low and resemble the data of Stock and Cucuel.[2]

Table 2. Mercury content of natural waters

Sample	Location	Hg ($\mu g/l$)	Reference
Hot spring	Kusatu	19 (av. of 4 samples)	This work
	Manza	<0.1 (av. of 5 samples)	This work
	Tamagawa	10	Iwasaki *et al.*[3]
		0.1 —0.5	Stock and Cucuel[2]
Mineral water		15	Krainov[5]
Sea water	Ramapo Deep, Japan Trench	0.08—0.15	Hamaguchi *et al.*[6]
	Minamata Bay	1.6 —3.6	Hosohara *et al.*[7]
	Sagami Bay	2.7	Ohta *et al.*[4]
River water	Tokyo-to	2.8	Ohta *et al.*[4]

Kusatu and Manza hot springs are located at the east and the west foot of the Shirane volcano, respectively. It was suggested by Noguchi *et al.*[8] that the Kusatu and Manza hot springs belong to different types of springs. Both Kusatu and Manza are of the strong-acid type, but the contents of many chemical constituents, such as alkali metals, magnesium, calcium, iron, arsenic, vanadium, chloride and sulfate, differ considerably; for example, chloride is more abundant in Kusatu (231—622 mg/*l*) than in Manza (139—197 mg/*l*).[8,9] However, the difference in mercury contents between Kusatu and Manza is excessively large compared to that of other constituents. This fact is of great interest and suggests a relationship between the mercury content and the mechanism by which the spring water wells out.

The authors wish to thank Mr. T. Araki, Tokyo Metropolitan University, for his useful comments.

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8) K. Noguchi, M. Ichikuni, T. Araki, T. Nishiido, A. Noguchi, and Y. Nakagawa, *Onsen Kagaku*, **17**, 9 (1966).
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