Copper, Lead, and Zinc Content of the Hot Springs of Japan.

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The occurrence of copper in a large number of hot springs of Japan has been found spectroscopically by K. Kimura[1] and in the present work a method for the determination of the minute quantities of copper in the large amounts of iron was studied and the method was applied to the determination of the element in a number of mineral springs of Japan. The copper, lead, and zinc content of some weak alkaline hot springs were also estimated by Fischer's method[2].

I. Determination of the Minute Quantities of Copper in the Mineral Springs. Add nitric acid to a 500 c.c. portion of the mineral water and boil to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) to slight excess and 5 c.c. of saturated ammonium carbonate solution. Warm and filter. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1) and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with dilute nitric acid and evaporate to dryness.

Dissolve the residue in nitric acid, ajust to *p*H 3 and titrate with the carbon tetrachloride solution of dithizone. The orange yellow colour of the carbon tetrachloride layer indicates the presence of silver. The silver is removed until the carbon tetrachloride layer turns to reddish violet. The carbon tetrachloride solution of dithizone is added with small portions until it remains green when vigorously shaken for several minutes. The amount of copper is obtained from the volume of the carbon tetrachloride solution of dithizone used to extract the reddish violet dithizone complex of copper. Each c.c. of the dithizone solution corresponded to 2.5γ of copper.

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(1) Not yet published.
(2) H. Fisher, *Angew. Chem.*, **47** (1934), 685; **50** (1937), 919. etc.

II. Copper Content of Some Mineral Springs of Japan.

The results from the quantitative determination of the minute traces of copper in some mineral springs of Japan is shown in Table 1. The iron content of some of these mineral springs was determined gravimetrically or by Mellor's colorimetric method, and the atomic ratio of copper to iron in the mineral springs was calculated (Table 2).

Table 1. Copper Content of Some Mineral Springs of Japan.

No.	Mineral spring	Prefecture	Temperature (°C)	*p*H	Copper Content	
					(γ/l.)	% (total residue.)
1	Kinbu	Yamanasi	—	—	68000	0.15
2	Kinkei	Totigi	10.0	2.4	1033	0.050
3	Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	93.0	2.0	163	0.0081
4	Hon-Onsen, Arima	Hyōgo	—	—	140	0.00084
5	Kinkei No. 2	Totigi	8.7	2.9	140	—
6	Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	87.8	2.2	90	0.0053
7	Yagendo, Arima.	Hyōgo	—	—	38	0.00035
8	Iron spring No. 1, Sinyu, Sukayu.	Aomori	—	—	12	—
9	Iron spring No. 2, Sinyu, Sukayu.	Aomori	—	—	10	—
10	Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	51.0	2.5	10	0.0010
11	Cold spring near Kinkei.	Totigi	6.0	6.5	6	—

Table 2. Atomic Ratio of Copper to Iron.

No.	Mineral Spring	Iron Content (g./l.)	Atomic Ratio of Copper to Iron. (Cu : Fe)
1	Kinbu	10.416	1 : 174
2	Kinkei	0.177	1 : 196
3	Daruma-Zigoku	0.016	1 : 112
4	Hon-Onsen	0.030	1 : 242
5	Kinkei No. 2	—	—
6	Yoemon-Yu	0.157	1 : 1980
7	Yagendo	—	—
8	Iron Spring No 1	0.00015	1 : 14
9	Iron Spring No. 2	—	—
10	Gongen-Yu	0.0068	1 : 777
11	Cold Spring near Kinkei	—	—

III. Copper, Lead, and Zinc Content of a Number of Weak Alkaline Hot Springs of Japan. The copper, lead, and zinc content of a number of weak alkaline hot springs in Japan were estimated by the colorimetric method. For the determination of lead, the colorimetric method which was described in the previous paper[3] was used. For the colorimetric determination of zinc, H. Fisher and G. Leopoldi's method[4] was adopted. The results of the experiments are shown in Table 3. Copper was detected in three samples (out of twelve samples), and lead in two samples (out of twelve samples). The traces of zinc were always found in these hot springs. The average zinc content of twelve samples was 13γ per litre.

Table 3. Copper, Lead, and Zinc Content of Some Hot Springs of Japan.

No.	Hot Spring	Prefecture	Temperature (°C)	*p*H	Cu	Pb (mg/l.)	Zn
1	Itō No. 3	Sizuoka	42.0	8.0	0.000	0.033	0.009
2	Itō No. 4	,,	42.0	8.0	0.003	0.000	0.016
3	Itō No. 8	,,	40.5	7.3	0.003	0.002	0.008
4	Itō No. 10	,,	38.0	7.4	0.002	0.000	0.010
5	Itō No. 13	,,	40.5	7.4	0.000	0.000	0.008
6	Moto-Yu, Kawazi	Totigi	43.0	7.7	0.000	0.000	0.009
7	Komoti-Yu, Kawazi	,,	43.0	7.7	0.000	0.000	0.021
8	Iwa-no-Yu, Kawazi	,,	42.5	7.7	0.000	0.000	0.027
9	Yakusi-Yu, Kawazi	,,	43.0	7.7	0.000	0.000	0.024
10	Hudō-no-Yu, Kawazi	,,	40.2	7.7	0.000	0.000	0.025
11	River Water, Ozikagawa, Kawazi	,,	15.5	7.1	0.000	0.002	0.036
12	Takara-no-Yu, Kinugawa	,,	55.5	8.0	0.000	0.000	0.012
13	Senami	Niigata	100.3	8.7	0.000	0.000	0.010
14	Sea Water, Itō	Sizuoka	—	—	0.009	0.004	0.006
15	Sea Water, Senami	Niigata	—	—	0.010	0.001	0.008

Summary.

(1) A method for the determination of the minute quantities of copper in the mineral springs was studied.

(2) Copper, lead, and zinc content of a number of hot springs of Japan were estimated.

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(3) K. Kuroda, this Bulletin, **15** (1940), 153.
(4) H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107** (1936), 241.