The Copper Content of the Hot Springs of Yunohanazawa, Hakone, Kanagawa Prefecture, and that of the Hot Springs of Osoreyama, Aomori Prefecture.

By Kazuo KURODA.

(Received February 22, 1941.)

In a previous paper(1), the author gave the results obtained, up to the time of publication, on the copper content of Japanese mineral springs. The copper content of a number of mineral springs was estimated by H. Fischer's diphenylthiocarbazone (dithizone) method(2). The writer's recent work, the results of which are given in this paper, concerns the determination of this element by the polarographic method.

(1) Determination of Copper by the Polarographic Method. For the polarographic determination of copper, the method of M. Shikata,

(1) K. Kuroda, this Bulletin, **15** (1940), 439.
(2) H. Fischer, *Angew. Chem.*, **47** (1934), 685; **50** (1937), 919.

I. Tachi, and N. Hozaki[3] was at first tried, but the writer failed to detect the presence of copper in the hot springs by this method. The second method adopted was that of K. Heller, G. Kuhla, and F. Machek[4], in which the copper in mineral waters is extracted with a carbon tetrachloride solution of dithizone. Notwithstanding the most scrupulous care exercised, the search ended in failure. The chief cause of failure probably lay in the presence of a large amount of iron in the mineral waters. After several trials, the following procedure, in which the large excess of iron is removed by ammonia prior to the extraction of copper by the carbon tetrachloride solution of dithizone, was found to be satisfactory for determining the minute traces of copper in acid alum-vitriol springs:

Add nitric acid to 500 c.c. of the mineral water and boil in order to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) in 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 nitric acid, and evaporate to dryness. Dissolve the residue in nitric acid, adjust to *p*H 3. Shake with successive 10 c.c. portions of the purified carbon tetrachloride solution of dithizone. Continue the extraction until the carbon tetrachloride layer remains green. Add 10 c.c. of conc. nitric acid and 10 mg. of sodium nitrate to the combined extracts and evaporate to dryness. Dissolve the residue in 10 c.c. of "Grundlösung A"[5] (170 g. $NaNO_3$+200 c.c. of gelatine solution (2%)+1800 c.c. H_2O). The solution is transferred to a small electrolysis vessel and polarographically examined. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amount of copper salt in "Grundlösung A".

The efficacy of the method was tested by adding known amounts of standard copper sulphate solution to 500 c.c. of water and submitting the solution to complete extraction, and polarographic determination with the following results:

Table 1.

No.	Height of wave (mm.)	Sensitivity
(1) 500 γ copper.	54	1/10
(2) Cu (500 γ) added to distilled water (500 c.c.). Extracted by dithizone.	53	1/10
(3) Cu (500 γ) added to the Yoemon-Yu spring water (500 c.c.). Extracted by dithizone.	54	1/10

(3) M. Shikata, I. Tachi and N. Hozaki, *Bull. Agr. Chem. Soc. Japan*, **3** (1927), 883.
(4) K. Heller, G. Kuhla and F. Machek, *Mikrochemie*, **23** (1937), 78.
(5) H. Hohn, "Chemische Analysen mit dem Polarographen," Berlin (1937), 41.

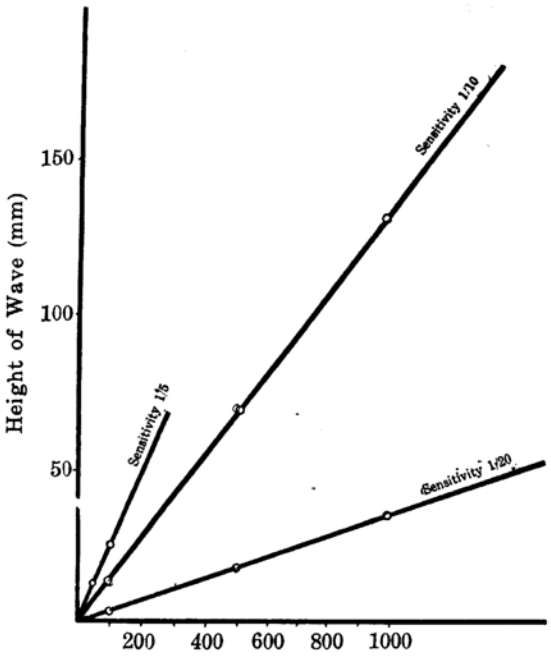

Fig. 1.

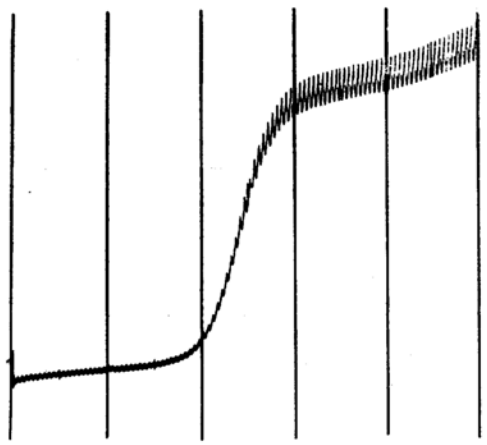

Fig. 2. Wave due to 500 γ of copper in "Grundlösung A". Sensitivity 1/10.

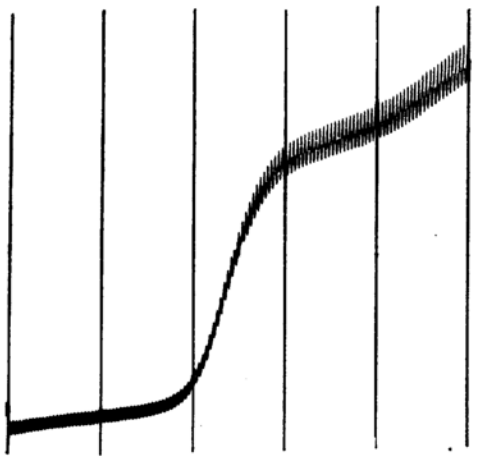

Fig. 3. 500 γ of copper was added to 500 c.c. of water. Extracted with carbon tetrachloride solution of diphenylthiocarbazone. "Grundlösung A". Sensitivity 1/10.

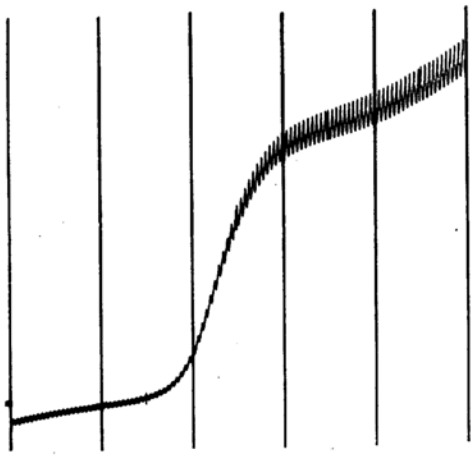

Fig. 4. 500 γ of copper was added to 500 c.c. of "Yoemon-Yu" spring. Extracted with carbon tetrachloride solution of diphenylthiocarbazone. "Grundlösung A". Sensitivity 1/10.

(2) Copper Content of the Hot Springs of Yunohanazawa, Hakone, Kanagawa Prefecture. The copper content of the Yoemon-Yu hot spring was polarographically estimated, with the result shown in Table 2, and

that of the hot springs of Yunohanazawa, estimated by H. Fischer's dithizone method[2], shown in Table 3.

The relations between temperature, *p*H, and the copper content are shown in Figs. 5, 6. The copper content is greater, the higher the temperature and the smaller the *p*H value of the hot spring. Table 4. shows the chemical composition of the Yoemon-Yu spring.

Table 2.

Hot spring	Date	Temp. (°C)	*p*H	Copper content	
				γ/l.	% (total residue)
Yoemon-Yu	Feb. 19, 1939	74.5	2.2	45	0.0026

Table 3.

Hot spring	Date	Copper content	
		γ/l.	% (total residue)
(1) Gongen-Yu	Aug. 20, 1938	7.1	0.0009
(2) Gongen-Yu	Aug. 26, 1939	10	0.0008
(3) Kōbō-Yu	Aug. 20, 1938	5	0.0005
(4) Yoemon-Yu	Aug. 20, 1938	90	0.0045
(5) Yoemon-Yu	Feb. 19, 1939	45	0.0026
(6) Daruma-Zigoku	Aug. 20, 1938	163	0.0081

Table 4.

Yoemon-Yu. Dec. 11 (1938) Temp. 78.0°C. *p*H 2.3	
K^+	0.0029 g./l.
Na^+	0.0329
Ca^{++}	0.1029
Mg^{++}	0.0131
Fe^{++}	0.0392
Al^{+++}	0.1204
SO_4^{--}	1.0366
Cl^-	0.0026
H_2SiO_3	0.3674
H_2S	trace
	1.7180 g./l.

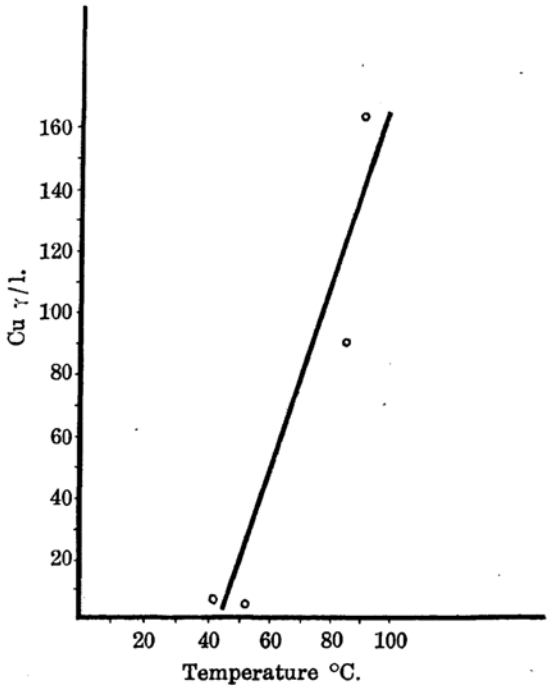

Fig. 5. Temperature and Copper Content.

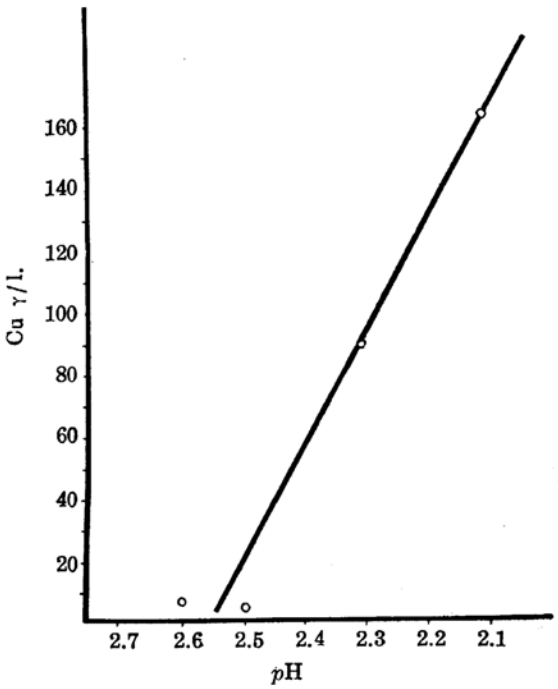

Fig. 6. *p*H and Copper Content.

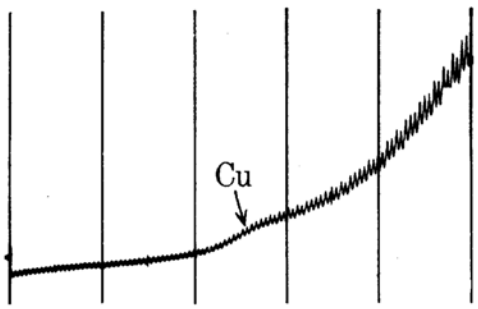

Fig. 7. Wave due to 45 γ of copper extracted from the "Yoemon-Yu" spring. "Grundlösung A". Sensitivity 1/10.

(3) Copper Content of the Hot Springs of Osoreyama, Aomori Prefecture. The temperature, *p*H, total residue, and the iron content of the hot springs of Osoreyama, Aomori prefecture, were measured in 1940. The copper content was also estimated polarographically, when it was found that it is very small compared with that of other acid springs in Japan, the reason for which is probably the presence of considerable hydrogen sulphide in these springs(6).

Table 5. Hot Springs of Osoreyama.

No.	Hot spring	Temp. °C.	*p*H	Total residue (g./l.)	Iron content	
					g./l.	% (total residue)
1	Yakusi-Yu	70.0	1.8	3.2	0.025	0.78
2	Hie-no-Yu	89.5	1.9	5.25	0.018	0.34
3	Hurutaki-no-Yu	79.0	2.0	5.30	0.030	0.57
4	Hanazome-no-Yu	68.5	2.0	1.5	0.0013	0.087
5	Sintaki-no-Yu No. 1	83.0	2.2	4.2	0.0034	0.081
6	Sintaki-no-Yu No. 2	60.8	2.4	3.1	0.015	0.48

(6) As is shown in Table 2, the copper content of the Gongen-Yu spring and the Kōbō-Yu spring is very small compared with that of other hot springs in Yunohanazawa, the reason for which is also the presence of considerable hydrogen sulphide in these springs. The Gongen-Yu spring contains 51.9 mg. and the Kōbō-Yu spring 33.1 mg. per litre of hydrogen sulphide.

Table 5.—(*Concluded*)

No.	Hot spring	Temp. °C	*p*H	Total residue. (g./l.)	Iron content.	
					g./l.	% (total residue)
7	Tikusyo-Zigoku	23.5	2.2	0.4	0.0022	0.55
8	Sioya-no-Zigoku	98.5	2.4	6.05	0.0101	0.167
9	Zigokudani No. 1	97.5	2.4	2.2	0 0042	0.19
10	Zigokudani No. 2	95.5	2.4	2.6	0.0038	0.15
11	Zigokudani No. 3	93.8	2.5	1.6	0 044	2.75
12	Zigokudani No. 4	75.5	2.4	4.8	0.0106	0.22
13	Bakutiuti-no-Zigoku	97.5	4.1	11.45	0.0017	0.015
14	Syurao-no-Zigoku	99.0	5.6	14.40	0.0001	0.007
15	Hokke-no-Zigoku	82.8	5.8	2.3	0.0001	0.004
16	Lake Osoreyama	22.0	3.0	0.1	0.0001	0.1
17	Drinking water	14.0	4.8	0.03	0.0001	0.3

Table 6. Copper Content of the Hot Springs of Osoreyama.

	γ/l.	% (total residue)
No. 6	30	0.00026
No. 13	20	0.00065

Summary.

A method for the polarographic estimation of copper is described. The copper content of the hot springs of Yunohanazawa, Hakone, Kanagawa prefecture, and that of Osoreyama, Aomori prefecture, are polarographically estimated.

The writer expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance in the course of this study. The expenses in connexion with this study were defrayed from a grant received by Prof. Kimura from the Japan Society for the Promotion of Scientific Research, to which last the writer's thanks are also due.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.