Zinc Content of the Hot Springs of Japan.

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Recently, considerable interest has been attached to the determination of the minute traces of rarer elements in natural waters and the observations have revealed the apparently universal distribution of heavy metals throughout the hydrosphere. A number of reports on the occurrence of zinc in sea water and in the mineral waters have already been published. The polarographic method for the determination of heavy metals such as copper, lead, nickel and zinc in the mineral waters has recently been quite well established by K. Heller, G. Kuhla and F. Machek.(1) P. R. Stout and his collaborators(2) have reported that the polarographic method is quite satisfactory for the determination of the minute traces of zinc in plant and animal tissues. The present author tested these methods and found that the following modified procedure was satisfactory for the determination of zinc in natural waters.

Method of Analysis. The method and apparatus used for the determination of zinc will be described in the following paragraphs.

(a) *Purification of the Diphenylthiocarbazone Carbon Tetrachloride Solution.* The solution of diphenylthiocarbazone in carbon tetrachloride was purified before use in the following manner:—Dissolve 0.1 g. of diphenylthiocarbazone in 100 ml. of carbon tetrachloride and wash the solution repeatedly with 6N hydrochloric acid in a separating funnel. Reject the aqueous layers, add 100 ml. of ammonia (5:95), shake, allow the layers to separate, reject the carbon tetrachloride layer. Add 100 ml. of carbon tetrachloride, acidify the aqueous layer with hydrochloric acid, draw off the carbon tetrachloride solution, and wash it with distilled water. This washed carbon tetrachloride solution constitutes the purified diphenylthiocarbazone reagent.

The amount of zinc derived from the glass bottle in which the mineral water was collected was found to be less than 10 γ per litre. The presence of zinc in water kept in the bottle for a long time was detected colori-

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(1) *Mikrochemie*, **23** (1937), 78.

(2) *Collection Czechoslov. Chem. Commun.* **10** (1938), 129.

metrically, but it was difficult to estimate the amount by the polarographic method. The glass vessels was always washed with diphenylthiocarbazone solution before use to remove the traces of zinc and other heavy metals.

(b) *Extraction of Zinc with Diphenylthiocarbazone.* Add 10 ml. of N ammonium citrate solution to a suitable quantity (100 ml. to 500 ml.) of the mineral water, adjust to pH 8.5 with ammonia using phenol red as indicator, and shake with successive 10 ml. portions of the purified carbon tetrachloride solution of diphenylthiocarbazone. Continue the extraction until the carbon tetrachloride layer remains green. Wash the combined extracts with dil. ammonia (1:1000), run the carbon tetrachloride solution into a seperating funnel, and shake with three separate 10 ml. portions of 6N hydrochloric acid. Combine the acid layers and wash them by pouring small quantities of carbon tetrachloride through the aqueous liquid without shaking. Add 10 mg. of sodium chloride to the acid solution, and evaporate to complete dryness.

(c) *Determination of Zinc by the Polarographic Method.* Dissolve the residue in water, add 1 ml. of N ammonium acetate solution and 1 ml. of 0.25N potassium thiocyanate solution, and make up the volume of the solution to 10 ml. with water. A part of the solution is brought to a small electrolysis vessel, freed from the air by a current of hydrogen and then polarographically examined. The amount of zinc present is obtained from the height of the polarographic wave at − 1.0 V. Fig. 1 shows a calibration curve obtained from various heights of wave due to various amounts of zinc salt in a solution which is 0.1N with respect to ammonium acetate and 0.25N to potassium thiocyanate, freed from atmospheric oxygen.

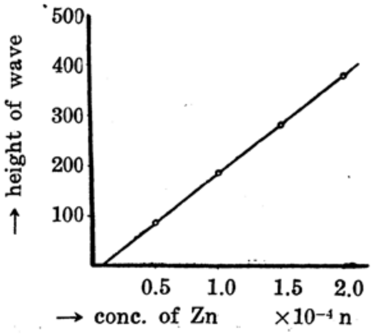

Fig. 1. The calibration curve for the wave due to zinc in a solution which is 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate.

Results. The efficacy of the method was first tested by adding known amounts of standard zinc sulphate solution to 50 ml. of water and submitting the solutions to the complete process of extraction and polarographic examination; the results obtained are shown in Table 1.

Table 1.

Zinc added (γ)	Zinc found (γ)	Error (γ)
32.7	31.6	−1.1
65.3	67.1	+1.8
98.0	93.3	−4.7
130.6	136.9	+6.3

Further experiments were made in which known quantities of zinc were added to 1000 ml. of the mineral water, and submitted to the complete process of extraction. The results are given in Table 2,

Table 2.

No.	Mineral Waters	Zinc added to 1000 ml. of the mineral water (γ)	Zinc found (γ)	Difference (Zinc Content) (γ)
1	Monkawa, Kanagawa Prefecture	0 65	113 176	113 111
2	Huezuka-Yu, Yunohanazawa, Kanagawa Prefecture.	0 130	20 154	20 24
3	Drinking water of Yunohanazawa	0 130	46 178	46 48

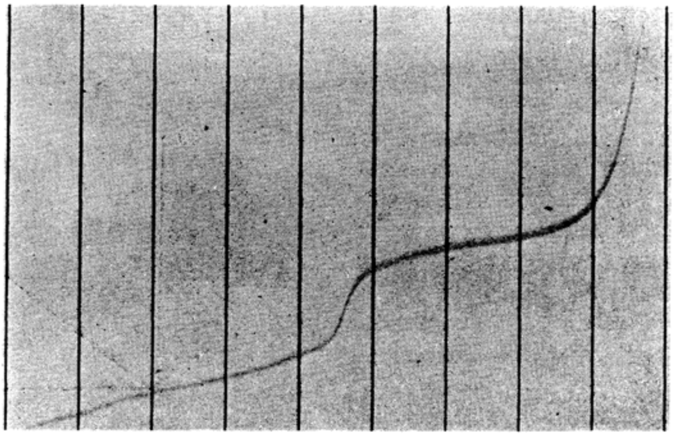

Fig. 2. Wave due to 68 γ of zinc extracted from the mineral water. (Military Sanatorium at the Misasa hot spring.) 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate. Sensitivity $\frac{1}{10}$. Curve starts from zero E.M.F. 4 V. accummulator.

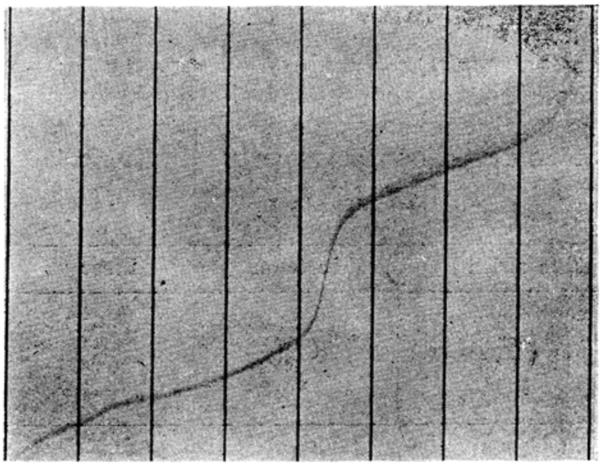

Fig. 3. Wave due to 112 γ of zinc extracted from the "Yuzawa No. 1" spring. 0.1 N with respect to ammonium acetate and 0.025 N to potassium thiocyanate. Sensitivity $\frac{1}{10}$. Curve starts from zero E.M.F. 4 V. accummulator.

The results of the determinations of the zinc contents, mainly of the hot springs of Japan, are collected in Table. 3.

Table 3.

Zinc Content of the Hot Springs of Japan.

No.	Hot Springs	Zinc Content.	
		(γ/l.)	% (total residue.)
(1)	Katakosi-Yu, Arima.	2010	0.0085
(2)	Yuzawa No. 10, Masutomi	284	0.019
(3)	Misasa Hotel, Misasa.	235	0.033
(4)	Yuzawa No. 1, Masutomi.	224	0.102
(5)	Kuridaira No. 1, Masutomi.	215	0.0060
(6)	Yuzawa No. 3, Masutomi.	164	0.082
(7)	Hana-no-Yu, Arima.	160	0.0009
(8)	Ikaho No. 1.	156	0.0014
(9)	Sanatorium at Misasa.	140	0.0045
(10)	Hon-Onsen. Arima.	140	0.0008
(11)	Military Sanatorium at Misasa.	136	0.0112
(12)	Yoemon-Yu, Yunohanazawa, Hakone.	132	0.0066
(13)	Yuzawa No. 5, Masutomi.	126	0.115
(14)	Daruma-Zigoku, Yunohanazawa.	120	0.0060
(15)	Wadamatuba, Masutomi.	113	0.0008
(16)	Monkawa.	113	0.0004
(17)	Yuzawa No. 4, Masutomi.	102	0.051
(18)	Yuzawa No. 7, Masutomi.	102	0.0065
(19)	Yagendo, Arima.	96	0.0009
(20)	Yuzawa No. 2, Masutomi.	88	0.0151
(21)	Sanatorium of the Medical College of Okayama at Misasa.	81	0.0053
(22)	Yuzawa No. 6, Masutomi.	80	0.022
(23)	Kinsentō, Masutomi.	80	0.0011
(24)	Ginsentō, (Huru-Yu), Masutomi.	80	0.0078
(25)	Ginsentō (Naka-no-Yu), Masutomi.	78	0.0080
(26)	Nanasigure.	73	0.0006
(27)	Bansuiro, Misasa.	66	0.0042
(28)	Yuzawa No. 9, Masutomi.	64	0.0042
(29)	Wadegawara (Simo-no-Yu), Masutomi.	64	0.0009
(30)	Yuzawa No. 8, Masutomi.	60	0.0036
(31)	Aziro.	46	0.0004
(32)	Higasiobi, Masutomi.	39	0.0004
(33)	Gantōhunsen, Masutomi.	35	0.0012
(34)	Kōbō-Yu, Yunohanazawa.	34	0.0034
(35)	Tuganerō, Masutomi.	26	0.0003
(36)	Umamitizawa, Masutomi.	26	0.0007
(37)	Gongen-Yu, Yunohanazawa.	25	0.0039
(38)	Huezuka-Yu, Yunohanazawa.	20	0.0033
(39)	Hii-no-Yu, Matunoyama.	less than 10	0.000
(40)	Tamagono-Yu, Matunoyama.	less than 10	0.000
(41)	Iriyamabe.	less than 10	0.000
(42)	Simokurohira,	less than 10	0.000
(43)	Hiukemizu, Masutomi.	less than 10	0.000
(44)	River water, Yunohanazawa.	less than 10	0.000
(45)	Sea water, Yosihama.	less than 10	0.000
(46)	Drinking water of Yunohanazawa.	46	0.0170
(47)	Tap water of Tokyo, Oct. 26, 1939.	116	
(48)	Tap water of Tokyo, Oct. 27, 1939.	133	
(49)	Tap water of New York.	124	
(50)	Distilled water.	less than 10	

Table 3. shows that the traces of zinc are widely distributed in the mineral waters in Japan. The mineral springs of Arima had the highest

zinc content. The average zinc content of forty-three samples was 0.013% (of the total residue), or 136 γ per litre. The presence of zinc in sea water was detected colorimetrically, but the author could not estimate the amount polarographically. The zinc content of sea water is considered to be less than 10 γ per litre.

Summary.

(1) The polarographic method was tested and found to be satisfactory for the determination of zinc in natural waters.

(2) The zinc content of a number of hot springs of Japan was polarographically estimated.

(3) The amount of zinc in sea water is considered to be less than 10 γ per litre.

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