## The Occurrence of Gallium in the Hot Springs of Japan.

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Gallium is widely distributed in nature in minute quantities, and it is detected spectroscopically in many rocks and minerals. It is, however, rarely reported in the mineral waters. J. Bardet<sup>(1)</sup> found this element in some French mineral waters, and S. Piña de Rubies and C. Sirvent d'Argent<sup>(2)</sup> in Spanish mineral waters. According to V. M. Goldschmidt,<sup>(3)</sup> the atomic ratio of gallium to aluminium in the aluminium minerals varies from 1:10 to 1:100000. The present author found the occurrence of gallium in a number of hot springs, mainly of acid alum-vitriol springs of Japan. Their gallium content was spectroscopically estimated.

Arc Spectrographic Estimation of Gallium. Pure gallium metal was dissolved in hydrochloric acid and the solutions containing 1, 0.1, 0.01, 0.001 and 0.0001 mg. of gallium per c.c. were prepared. Sodium chloride (10 mg.) was added to 1 c.c. of each solution, and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excitation. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001 and 0.0001 mg. of gallium respectively. The Hilger spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 1. In this table, s signifies that the line in question is strong, w that it is weak and F that it is faintly visible.

<sup>(1)</sup> J. Bardet, Compt. rend. 157 (1913), 224.

<sup>(2)</sup> S. Piña de Rubies, C. Sirvent d'Argent, Anal s soc. españ. fís. quím. 29 (1931), 235: Chem. Abstracts, 25 (1931), 3104.

<sup>(3)</sup> V. M. Goldschmidt, Cl. Peters, Nachr. Ges. Göttingen, Math.-physik. Klasse 1931, 165-85 (1931).

λ <b>(Å)</b>	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.	0.0001 mg
2255.03	F	, .			
2259.23	F				
2294.20	w	F			
2297.87	w	F			
2338.60	s	w			
2371.33	s	w			
2418.70	s	w	F		
2450.08	s	s	w .		
2500.71	s	s	w	F	
2659.87	s	s	w	F	
2719.66	S	s	w w	$\mathbf{F}$	
2874.24	s	s	· s	S	F
2943.7	S	s	s	S	w
2944.18	S	s	w .	F	
4033.01	s	. S	s	<b>F</b>	
4172 06	S	s	w ·	F	

Table 1. Spectral Lines at Different Concentrations.

Gallium Content of the Hot Springs of Japan. Aluminium oxide (10 mg.) obtained from the suitable quantities (5 to 50 c.c.) of the mineral water was subjected to arc excitation. The following gallium lines were found (Table 2). Table 2 shows that seven samples (out of eleven samples) contained about  $0.1~\gamma$  of gallium in 10 mg. of aluminium oxide. The gallium content of the hot springs was calculated from their aluminium content. The results are shown in Table 2 and Table 3.

Except the hot springs of Yunohanazawa, gallium was always found in the above-mentioned acid alum-vitriol springs of Japan. The atomic

Hot Spring		Prefecture	2874.24 Å	2943.7 Å
(1)	Kinbu.	Yamanasi		w
(2)	Seki-no-Yu, Kusatu.	Gumma	w	s
(3)	Sirahata-no-Yu, Kusatu.	Gumma	F (?)	w
(4)	Zizo-no-Yu, Kusatu.	Gumma	_	w
(5)	Wasi-no-Yu, Kusatu.	Gumma		w
(6)	Takayu.	Yamagata	_	E
(7)	Kinkei.	Totigi		_
(8)	Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	_	_
(9)	Kōbō-Yu, Yunohanazawa, Hakone.	Kanagawa	_	. —
(10)	Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	_	_
(11)	Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	_	

Table 2. Spectral Lines of Gallium.

Table 3. Gallium Content of the Hot springs of Japan.

	Hot Spring	Gallium Contents (g./l.)		
(1)	Kinbu.	1~ 5×10⁻⁵		
(2)	Seki-no-Yu, Kusatu.	$5\sim 10\times 10^{-6}$		
(3)	Sirahata-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$		
(4)	Zizo-no-Yu, Kusatu.	$1 \sim 5 \times 10^{-6}$		
(5)	Wasi-no-Yu, Kusatu.	1~ 5×10⁻6		
(6)	Takayu.	$1 \sim 5 \times 10^{-6}$		
(7)	Kinkei.	$5\sim 10\times 10^{-7}$		
(8)	Gongen-Yu, Yunohanazawa.	less than $10^{-7}$		
(9)	Kōbō-Yu, Yunohanazawa.	less than $10^{-7}$		
(10)	Yoemon-Yu, Yunohanazawa.	less than $10^{-7}$		
(11)	Daruma-Zigoku, Yunohanazawa.	less than $10^{-7}$		

ratio of gallium to aluminium in the hot springs is considered to be 1:100000. Expressed in percentages to total residue, the gallium content of these hot springs is between 0.001 and 0.00001.

## Summary.

- (1) An arc spectrographic detection and estimation of gallium was studied.
- (2) The gallium content of a number of hot springs of Japan was estimated.

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