Vanadium, Chromium, and Molybdenum Contents of the Hot Springs of Japan.

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Aside from their well known mineral combinations, vanadium, chromium and molydenum have long been known to occur in a great variety of rocks. They have been detected, however, rarely in mineral waters. The occurrence of vanadium, chromium and molybdenum in a large number of Japanese mineral waters has been recently found spectroscopically by Prof. K. Kimura, and their contents in the hot springs of Yunohanazawa, Hakone, Kanagawa Prefecture have been estimated by S. Oana.[1] In the present paper the author describes the results from the quantitative estimations of these elements in a number of hot springs of Japan.

Methods of Analysis. For the determinations of vanadium, chromium and molybdenum, Sandell's colorimetric method[2] was adopted. The analytical procedures will be briefly described in the following paragraphs.

(1) *Decomposition of Sample.* 2 to 5 g. of dry residue were first fused with anhydrous sodium carbonate. The melt was leached with water and ethyl alcohol was added to reduce MnO_4^{--}. Then it was filtered. The aqueous extract contains CrO_4^{--}, VO_3^- and MoO_4^{--}, and the volume was made up to 100 c.c.

(2) *Vanadium.* A 30 c.c. portion was neutralized to methyl orange with 4N sulphuric acid and, after the addition of 8-hydroxyquinoline, vanadium was extracted by shaking with chloroform. The residue obtained by evaporating the chloroform solution was fused again with anhydrous sodium carbonate and the aqueous extract of this melt was treated with phosphotungstic acid: the yellow to orange colour was compared with that obtained with standard vanadium solutions.

(3) *Chromium.* A 10 c.c. portion was transferred to a small separting funnel, and neutralized to methyl orange with 4N sulphuric acid without using an indicator and, after the addition of 8-hydroxyquinoline, vanadium was removed by shaking with chloroform. Diphenylcarbazide and sulphuric acid were added: the red-violet colour was compared with that obtained with standard chromium solutions.

(4) *Molybdenum.* A 50 c.c. portion was transferred to a separating funnel. Concentrated hydrochloric acid, potassium thiocyanate solution and stannous chloride solution were added. The red-brown molybdenum thiocyanate was extracted with ether and the colour was compared with that obtained with standard molybdenum solutions.

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(1) Not yet published.
(2) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8** (1936), 336.

The Results of the Analyses. The results of the analyses are shown in Table 1.

Table 1. Vanadium Chromium and Molybdenum Contents of the Hot Springs of Japan.

Hot Springs	Parts per million of the mineral water			% (per dry residue)		
	V	Cr	Mo	V	Cr	Mo
(1) Mito, Sizuoka Prefecture	0.247	0.015	0.005	0.0190	0.0012	0.0004
(2) "Daruma-Zigoku", Yunohanazawa, Hakone, Kanagawa Prefecture	0.220	0.008	0.002	0.0105	0.0004	0.0001
(3) Monkawa, Kanagawa Prefecture	0.208	0.000	0.005	0.0007	0.0000	0.00002
(4) "Kōbō-Yu", Yunohanzawa, Hakone, Kanagawa Prefecture	0.079	0.000	0.0004	0.0079	0.0000	0.00004
(5) Matunoyama, Niigata Prefecture	0.059	0.000	0.011	0.0004	0.0000	0.00008
(6) Nanasigure, Iwate Prefecture	0.054	0.000	0.010	0.0004	0.0000	0.00008
(7) Kinkei, Totigi Prefecture	0.051	0.073	0.002	0.0024	0.0035	0.0001
(8) "Umi-Zigoku", Beppu, Ōita Prefecture	0.022	0.003	0.001	0.0006	0.0001	0.00003
(9) Murasugi No. 3, Niigata Prefecture	0.000	0.000	0.016	0.0000	0.0000	0.0095

The hot springs of Mito had the highest vanadium content, 0.0190% (per dry residue) and the mineral waters of Murasugi No. 3 the lowest, less than 0.001% (per dry residue). The average vanadium content of nine samples was 0.005% (per dry residue). It is supposed that vanadium is associated with iron and widely distributed in the mineral waters. The mineral waters of Kinkei had the highest chromium content, 0.0035% (per dry residue). Five samples (out of nine samples) contained less than 0.0001% (per dry residue) of chromium and the author could not detect it colorimetrically. Novokhatsky and Kalinin[3] reported molybdenum to be present in a number of hot springs in the Transilian Alatau Range in quantities varying from 0.001 to 0.06% (per dry residue). It is shown in Table 1 that the small amounts of molybdenum are widely distributed in the mineral waters of Japan. The Mineral waters of Murasugi No. 3 had the highest molybdenum content, 0.0095% (per dry residue). The molybdenum content of Murasugi No. 3 was also spectroscopically estimated by the present author to be 0.01% (per dry residue), as described below.

Arc Spectrographic Detection and Estimation of Molybdenum in the Mineral Waters of Murasugi No. 3. Prof. K. Kimura found the occurrence of molybdenum in the mineral waters of Murasugi No. 3 and an arc spectrographic estimation of the element was attempted by the present author. Solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg. of molybdenum per c.c. were prepared. 10 mg. of sodium chloride 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 excita-

(3) *Compt. rend. acad. sci. U.R.S.S.*, **22** (1939), 323.

tion. The Hilger quartz spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 2. In this table, S signifies that the line in question is strong, W that it is weak and F that it is faintly visible.

Table 2. Spectral Lines at Different Concentrations.

λ (Å)	1 mg.	0.1 mg.	0 01 mg.	0.001 mg.	0.0001 mg.	0.00001 mg.
3041.7	W	W				
3112.1	W	W	F	F		
3132 6	S	S	W	W	F	F
3158 2	S	S	W			
3170.3	S	S	W	W	W	F
3194.0	S	S	W	F		
3208.9	S	S	W	W	W	F
3256.2	W	W				
3289.0	W	W				
3290.8	W	W				
3325.7	W	W				
3327 3	W	W				
3340.2	W					
3344.8	W	W				
3347.3	W	F				
3358.1	W	W				
3361.4	W	W				
3363 8	W	W				
3379.9	W	W				
3382.5	W	W				
3384.6	W	W	W	W	W	F
3404.4	F					
3405.9	W	W				
3418 5	F					
3447.1	W	W	F			

500 c.c. of water sample was evaporated to complete dryness. Finely powdered residue in ten milligram portions was subjected to arc excitation. The following molybdenum lines were always found.

λ (Å)	Intensity
3112.1	faint
3132.6	weak
3170.3	weak
3194.0	weak
3208.9	weak
3384.6	weak

This would seem to indicate that 0.001 mg. of molybdenum was present in the zone of excitation. Expressed in percentages,[4] the molybdenum con-

(4) Expressed in terms of parts per million of the mineral water it is supposed to be 0.02.

tent in the total residue of the mineral waters of Murasugi No. 3 is estimated to be 0.01, which is quite close to the value obtained by the colorimetric method.

Summary.

(1) The vanadium, chromium and molybdenum contents in a number of hot springs of Japan were estimated.

(2) The molybdenum content of the mineral waters of Murasugi No. 3 was spectroscopically estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. It is also the author's pleasant duty to acknowledge the valuable advice offered by Mr. S. Oana. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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