The Occurence of Thallium in Minerals in Japan

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Introduction

Thallium is one of the geochemically high dispertive elements.⁽¹⁾ Some minerals containing thallium as their principal constituent are known to be secondary minerals and very rare.⁽²⁾ Besides its occurrence in these minerals, thallium is sometimes found concentrated in an intermixture of copper,⁽³⁾ iron⁽⁴⁾ and zinc⁽⁵⁾ sulfide ores. Thus, the flue-dust and chamber muds in refineries or sulfuric acid factories processing these ores are rather important as a technical source of thallium as studied by many workers.

Prof. K. Kimura and Y. Koyama⁽⁶⁾ have investigated the thallium content in about eighty minerals in Japan by their semi-quantitative spectroscopic method. The author together with the above had hoped to investigate further the occurrence of thallium in these minerals and ores. Results of about 30 samples spectroscopically tested by the above method proposed by the two workers and the results of some which were chemically determined by the authors' method by using hexammine cobalti-trichloride as precipitant⁽⁷⁾ to thallium, will be reported here.

Experimental

Spectroscopic Test Thallium has been spectroscopically determined by the following table proposed by the two workers.

Experimental Conditions Spectrograph: E 2 Type Spectrograph, Adam Hilger Co. Ltd., London.

Electrode: Electrolyzed copper rod (diameter 3 mm.). Diameter of hole into which the sample is inserted is 1 mm. and depths, 3 to 4 mm.

Current: Gradually increased up to 7 amperes during the first 30 seconds, maintaining 7 amperes for 40 seconds.

Dry plate: Process, panchromatic, Fuji Photograph Ind. Co. Ltd., Japan.

Developing: Developed at 3 min., 18°C with a special developer for the process plate above mentioned.

Table 1.
Relation between thallium content and intensity of its spectrum line*

Wave length	Thallium content (%)			
Å	1	0.1	0.01	0.001
3775.7	s	s	s	w
3229.8	w	—	—	—
2921.5	w · w	—	—	—
2918.3	s	w	w · w	—
2826.2	w · w	—	—	—
2710.7	?	—	—	—
2709.3	w · w	—	—	—
2379.6	w	—	—	—

* Cited from the report by K. Kimura and Y. Koyama (*J. Chem. Soc. Japan*, **57**, 1190 (1936))

Analytical Test Some of these samples spectroscopically found abundant in thallium were analyzed chemically. The sample about 10 g. powdered (100 mesh), dried at 105°C and made into a solution with the acid mixture was then determined closely following the author's method.

Experimental results

Analytical results are shown in Table 2.

Conclusion

By comparing the spectroscopical with the analytical results, it may be stated that the method proposed by Prof. K. Kimura *et al* can be utilized as a rapid and good method of the determination of thallium. The author's method in testing ores is also satisfactory, being distinctive in that it is hazardless and speedy, a condition not known in any other method of the past.

V.M. Goldschmidt⁽⁸⁾ had classified thallium as a chalkophile element, and it had been stated by Berg⁽⁹⁾ that thallium occurs in zincblende and iron sulfide ore, concentrated from the hydrothermal rest-solution in geochemical crystallization. Though a large number of the sample has not as yet been tested, the same results have been obtained, being distinctively so with markasite and pyrite. But in copper sulfide ore, thallium is either not found at all or else found in a very small amount.

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Table 2

Thallium content in minerals

	Sample	Occurrence	Line detected	Content Spectroscopically	Content Chemically	Other constituent (in order of intensity)
1.	Markasite	Mori, Yamagata Pref.	3775.72(s) 2918.32(w)	0.1 %	0.085 %	Fe, Si, Al.
2.	Markasite	Tomimoto Yamagata Pref.	——	——	——	Fe, Si.
3.	Enarzite	Shimokita Oage, Aomori Pref.	3775.72(s) 2918.32(w)	0.1	0.056	Fe, Si.
4.	Markasite No. 1	Shimokita Oage, Aomori Pref.	3775.72(s) 2918.32(w)	0.1	——	Fe, Bi, Pb, As, Mn.
5.	No. 2	„	3775.72(W.W)	0.1 to 0.01	——	Pb, Fe.
6.	No. 3	„	3775.72(s) 2918.32(?)	<0.1	——	Pb, Fe, As.
7.	No. 4	„	3775.72(s) 2918.32(?)	<0.1	——	Fe, Si.
8.	Pyrite	Ochiaizawa bed, Hanaoka, Akita Pref	not tested	——	0.007	
9.	Black ore	Nishikanon bed, Hanaoka, Akita Pref.	not tested	——	0.001	
10.	Markasite	Kamiyama bed, Hanaoka, Akita Pref.	not tested	——	0.125	
11.	Zinc blend	Yunohanazawa, Akita Pref.	3775.72 2918.32(w)	0.1 to 0.01	0.070	Zn, Si, Pb.
12.	Copper ore No. 1	Doyashiki Hanaoka, Akita Pref.	not tested	——	0.005	
13.	No. 2 concentrates	„	not tested	——	0.024	
14.	No. 3	„	not tested	——	0.003	
15.	Markasite (in brown coal)	Agi, Gifu Pref.	——	——	——	Fe, Si, Mg.
16.	Black ore	Owani, Aomori Pref.	——	——	——	Zn, Pb, Mg.
17.	Covelin	Masutomi, Yamanashi Pref.	3775.72(?)	<0.001	——	Cu, Si.
18.	Markasite	„	——	——	——	Fe, Si.
19.	Enarzite	„	——	——	——	Cu, As.
20.	Ruzonite	„	——	——	——	Cu, Sb, As, Sn.
21.	Pyrite	Nishikanon bed, Hanaoka, Akita Pref.	not tested	——	0.007	
22.	Bismuth ore	Togane, Gifu Pref.	3775.72(?)	<0.001	——	Bi, Mo, Ca, Pb, Al, W, Sn.
23.	Markasite	Masutomi, Yamanashi Pref.	3775.72 2918.32(w.w)	0.1	not tested	Fe, Si.
24.	Zinc blend No. 1	Okurazawa, Akita Pref.	3775.72(w.w)	0.001	——	Zn, Si, Na, Pb, Al.
25.	No. 2	„	3375.72(w.w)	0.001	——	Zn, Si, Na, Pb, Al.
26.	Bismuthinite	Ebisu, Gifu Pref.	——	——	——	
27.	Bithmuth ore	Hohen, Yamaguchi Pref.	——	——	——	Fe, Si, Mg.
28.	Nature Bismuth	Ebisu, Gifu Pref.	3775.72(w) 2918.32(w)	0.1 to 0.001	not tested	Bi, Al, Mo, W, Sn, Zn, Si, Ag, As.
29.	Lead ore No. 1	Taishu (Akusuidani); Nagasaki Pref.	——	——	——	Fe, Si, Pb, Mg.
30.	No. 2	Taishu (Sasu bed No. 6); Nagasaki Pref.	3775.72(?)	0.001	——	Fe, Zn, Pb, Mg.

Thallium in natural bismuth and its ore could not be found in Ebisu mine formerly reported by Prof. K. Kimura and K. Koyama as a source of abundant thallium in zinc-blende and others. On the contrary it is remarkable that these samples abundant in thallium have been found in the Northeastern District (Tohoku-Chiho) of Japan.

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