The Determination of Thallium in Flue-Dust and Lead Chamber Muds.

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(Received March 31, 1949.)

Introduction. Thallium is one of the rare elements found as an essential constituent in any substantial quantity in only two or three minerals. But in small proportions thallium is widely distributed in natural rocks and minerals such as carnalite, alunite, copper and iron sulphide, zinc blend and braunite. When they are used as in industries, thallium is concentrated in chamber muds and flue-dust giving rise to a determinable amount. Thus thallium is more usually found accumulated in these substances rather than as a constituent of minerals.(1)

Thallium was discovered spectroscopically in chamber muds by Crookes and Lamy(2) independently in 1861. Since then various workers had succeeded in determining the thallium content in both chamber muds and flue-dust.

When the determination of thallium content in such samples was undertaken for the purpose of securing the most abundant technical source of the element, the author reviewed the methods applied hitherto. But they were found to be unsatisfactory in some respects from the reason that they require an elaborate process of separation due to the

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(1) W. T. Roepper, *Am. Jour. Science*, (2), **35** (1863), 421; R. Böttger, *Lieb. Ann.*, **126** (1863), 177, 266; F. Wöhler, *Lieb. Ann.*, **142** (1867), 263; T. Carstanjen, *J. Prakt. Chem.*, **102** (1867), 65: N. N. Melnikow, *Uspeki. Chim.*, **4** (1935), 256; A. V. Petar, *U. S. Bur. Mines Information*, circular No. **6453** (1931), 31.

(2) W. Crookes, *Chem. N.*, **3** (1861), 193, 303; *J. Chem. Soc.*, **17** (1864), 115; *Chem. N.*, **7** (1863), 133; A. Lamy, *Compt. rend.*, **54** (1862), 1255; *Lieb. Ann.*, **124** (1862), 215.

presence of many metals, such as copper, iron, zinc and lead, etc., occurring in quantities hundreds and thousands times greater than thallium.

However, among these methods proposed up to the present date the one suggested by Spacu and Pope(3) appeared to be the most effective and an improvement upon it was successfully undertaken by the author as was already described in detail in a previous report.(4)

Thus a minute amount of thallium as slight as 0.001% can be determined by this improved method with fairly good results. The results obtained from about 45 samples of chamber muds and flue-dust collected from sulfuric acid plants and refineries in Japan are described in this report.

Experiment. (a) Moisture: Moisture content was determined by placing a sample in original state in an air oven for 2 hours and drying at 105°C. Several samples were hygroscopic after drying, probably owing to the presence of free sulfuric acid.

(b) Color: The color of a sample was compared with the soil color table published by Japan Forestry Society in accordance with the National Color Standard.

(c) Specific gravity: The specific gravity is determined by measuring the sample already dried (105°C) with a pycnometer.

(d) Thallium determination: This determination has already been given in detail by the author in a previous report but will be briefly recorded in the following. According to the amount of thallium content to be expected in the sample, approximately 30 g. to 50 g. of the dried powdered sample is taken and dissolved by heating with an acid mixture, consisting of one part of H_2O, two parts each of HCl and HNO_3 and four parts of H_2SO_4, being mixed in the order named.

Heating is continued until all traces of copious sulfur dioxide fumes have ceased to appear. The residual cake is disintegrated with 1 N hot sulfuric acid solution, to which it is preferable that a few drops of H_2O_2 is added to reduce any Tl^{+++} that may have been formed in the process. After standing for a few minutes this is thoroughly extracted and neutralized first with sodium hydroxide followed by sodium carbonate solution until carbon dioxide has not been evolved.

Next, sulfur dioxide is passed through the solution until it cools. After filtration the filtrate is heated to boiling to expel sulfur dioxide and acidified to about 1 N hydrochloric acid. Particles of potassium chlorate are added and then 0.5 g. of ammonium chloride, the addition of which is effective in determining a minute amount of thallium. Heating is continued until the filtrated solution is boiled down to half its bulk.

If saturated cobalti-hexammine trichloride solution is added after cooling and filtering, a heavy orange yellow precipitate of $Co(NH_3)_6(TlCl_6)$ will instantaneously appear.

This precipitate is pure enough to be weighed on a glass filter (G4, for fine precipitate), assured to constant weight, after it has been washed thoroughly with 2% HCl solution followed by three times each of 5 ml. 95% alcohol and 5 ml. ether and dried at 105°C. Thallium content is calculated from the following equation:

$$\mathrm{Tl}\ (\%) = \frac{\text{Weight of precipitate} \times 0.35346}{\text{Weight of sample taken}} \times 100\ (\%)$$

(e) Reproducibility: The spectroscopic analysis shows that flue-dust and chamber muds contain a large amount of diverse metals, for example, such as the following:

No. 1. Zn, Cu, Pb, Fe, As, K (major), Ca, Al, Na, Si, Ti, Bi, Mg, Tl, Ge, Cd, Sb, Ag, Ni, Mo (minor).

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(3) G. Spacu and A. Pope, *Z. anal. Chem.*, **102** (1940), 322.

(4) Y. Murakami. *This Bulletin*. **22** (1949), 206.

No. 2. Fe, Zn, Ca, Al, Pb, Sb, Mg, Si, Cu, As (major), Bi, Tl, Ba, Sn, K, Na, Sb, Si, In, Ge, Ag, Ti, Co, Cd, Mn.

No. 3. Zn, Pb, Sn, K, Na, Sb, As (major), Tl, Fe, In, Ca, Al, Ag, Cu, Cd, Mo, Mg, Bi, Si.

The interference of these metals in the determination of thallium had been thoroughly tested as already reported and no fatal interference has been observed. To ascertain the reproducibility of this method, three main samples of flue-dust were selected for this test upon reference to the results obtained from the spectroscopic test and a known amount of thallium was added to the samples. Thallium was determined by the newly proposed method and the result is shown in Table 1.

Table 1.
Reproducibility

Sample	Thallium added (g.)	Thallium complex (g.)	Thallium found (g.)	Thallium calculated (g.)	Difference (g.)
1. Flue-dust abundant in copper	$\triangle\overline{0.01149}$	0.0202 0.0530	0.00714 0.01873	$\triangle\overline{0.01863}$	$\triangle\overline{+0.00010}$
2. Flue-dust abundant in iron	$\triangle\overline{0.01149}$	0.0255 0.0581	0.00901 0.02054	$\triangle\overline{0.02050}$	$\triangle\overline{+0.00004}$
3. Flue-dust abundant both in copper and iron	$\triangle\overline{9.01149}$	0.0171 0.0497	0 00604 0.01761	$\triangle\overline{0.01753}$	$\triangle\overline{+0.00008}$

Complete satisfaction was obtained from this method: first, it is not hazardous owing to the unnecessity of a preliminary separation of metals: secondly, it is most successfully effective in the determination of small quantities of thallium as little as 0.01%: and thirdly, the results obtained show a minimum average deviation, being less than 1%.

Results. The object was to determine the minute amounts of thallium in 46 samples of flue-dust and chamber muds collected from sulfuric acid plants, fertilizer factories and refineries in Japan. The results are shown in Table 2.

Table 2.
Thallium content in flue-dust and chamber muds

No.	Company	Factory	Moisture (%)	Sp. gr.	Thallium content (%)	Remarks
1	Dainippon Kogyo	Hasei Kogyo	10.44	4.65	0.105	
2	Sumitomo Met. Ind. Co., Ltd.	Gensan Factory	1.23	0.70	0.089	Cottrell dust
3	Nitto Chem. Ind. Co., Ltd.	Yokohama Factory	4.54	3.39	0.042	Cottrell dust
4	Konoshima Chem. Ind. Co., Ltd.	Konoshima Factory	4.04	3.44	0.120	
5	Nippon Soda Ind. Co., Ltd.	Aizu Factory	3.59	3.47	0.016	Cottrell dust
6	Asahi Chem. Ind. K.K.	----	0.52	2.09	0.025	
7	Nippon Kogyo K.K.	Saganoseki Refinery	3.87	2.10	0.169	Cottrell dust

Table 2. (*continued.*)

No.	Company	Factory	Moisture (%)	Sp. gr.	Thallium content (%)	Remarks
8	Nitto Ryuso K.K.	Tokyo Factory	6.84	3.18	0.021	
9	Toa Kagaku Seiren K.K.	Osaka Factory	9.97	3.12	0.038	Cottrell dust
10	Nippon Jukagaku K.K.	—	2.97	3.08	0.000	
11	Nippon Hydrogen Ind. Co., Ltd.	Onahama Factory	8.14	2.86	0.115	Cottrell dust
12	Nippon Kogyo K.K.	Toyama Factory	3.05	3.05	0.227	Cottrell dust
13	Showa Denko K.K.	Kawasaki Factory	9.61	3.57	0.281	Sulfide ore
14	Nitto Ryuso K.K.	Niigata Factory	7.62	2.98	0.000	
15	Niigata Sulfuric Acid Co., Ltd.	Niigata Factory	9.15	4.15	0.029	Cottrell dust
16	Sansei Kogyo K.K.	Choko Refinery	2.38	4.49	0.031	Chimney dust
17	Teikoku Kohatsu K.K.	Murakami Refinery	1.12	5.33	0.023	Dust chamber
18	Toa Kogyo K.K.	Osaka Factory	5.58	3.54	0.059	
19	Ishihara Kogyo K.K.	Yokkaichi Factory	13.92	5.98	0.010	Smelting furnace
20	Nippon Kogyo K.K.	Chinnanbo Refinery	1.37	0.80	0.074	
21	Nippon Kogyo K.K.	Nagoya Factory	6.76	3.42	0.062	Sulfide ore
23	Furukawa Min. Ind. Co., Ltd.	Nagamatsu Factory	1.67	1.26	0.020	Chamber muds
25	Nippon Kogyo K.K.	Ouji Factory	3.48	3.46	0.006	Sulfide ore (Osaruzawa)
26	Nippon Kogyo K.K.	Ouji Factory	7.43	3.58	0.040	Sulfide ore (Hitachi)
27	Nippon Kogyo K.K.	Ouji Factory	5.23	2.87	0.010	Sulfide ore (Hitachi and Matsuo)
28	Nippon Kogyo K.K.	Chinnanbe Refinery	1.38	0.71	0.012	Hourin mine
29	Mitsui Min. Ind. Co., Ltd.	Nihi Refinery	4.70	1.21	0.091	
30	Sumitomo Min. Ind. Co., Ltd.	Kunitomi Refinery	8.11	0.63	0.007	
32	Nitchitsu Kogyo Kaihatsu K.K.	Konan Refinery	1.90	2.70	0.084	Copper ore
33	Tohoku Hiryo K.K.	Akita Factory	7.05	3.68	0.005	Chamber muds
34	Mitsubishi Kogyo K.K.	Osaruzawa Refinery	6.31	1.76	0.073	
35	Nitto Ryuso K.K.	Shimonoseki Factory	33.86	1.06	0.006	Chamber muds
36	Kureha Boseki K.K.	Nishiki Factory	12.32	3.24	0.053	Sulfuric acid plant

Table 2. (*continued.*)

No.	Company	Factory	Moisture (%)	Sp. gr.	Thallium content (%)	Remarks
41	Fujita Min. Ind. Co., Ltd.	Kosaka Factory	2.56	3.54	0.003	Smelting Furnace
42	Fujita Min. Ind. Co., Ltd.	Kosaka Factory	17.93	4.78	0.104	Converter Furnace
43	Yahagi Chem. Ind. Co., Ltd.	Nagoya Factory	3.75	3.48	0.019	
44	Niigata Sulfuric Acid Ind. Co.	Yokohama Factory	5.65	3.22	0.001	Cottrell dust
45	Nitto Chem. Ind. Co., Ltd.	Nakagawa Factory	4.96	3.85	0.033	Sulfuric acid plant (contact process)
46	Nakagawa Chem. Ind. Co., Ltd.	Nakagawa Factory	6.87	3.52	0.000	Sulfuric acid plant (lead chamber)
47	Toyo Koatsu Kogyo K.K.	Omuda Factory	2.10	1.74	0.002	Hot Cottrell dust
48	Toyo Koatsu Kogyo K.K.	Omuda Factory	4.82	4.41	0.064	Mist Cottrell dust
49	Mitsubishi Min. Ind. Co., Ltd.	Hosonokura Refinery	3.04	1.33	0.039	Cottrell dust (lead)
52	Tagi Seihijo Co., Ltd.	——	17.44	1.33	0.040	Sulfuric acid plant
53	Tagi Seihijo Co., Ltd.	——	21.69	2.92	0.046	Sulfuric acid plant
60	Nitchitsu Kogyo Kaihatsu K.K.	Konan Refinery	1.19	1.38	0.033	Cottrell dust (lead)
61	Mitsubishi Min. Ind. Co., Ltd.	Hosonokura Refinery	6.24	3.66	0.070	Zinc ore

Conclusion. The spectroscopic detection of minute quantities of thallium in the flué-dust and chamber muds was frequently undertaken by several workers but its chemical determination was rare. And in the latter case, the thallium content determined chemically had been exceedingly large,(5) a thing which seldom occurs. For instance in one of the results a value as large as 6% had been reported. Such minute quantities of thallium as determined chemically by the author is impossible to be determined with any other method used hitherto.

Reasons for the superiority of the author's method responsible for the good result are attributed to the following: (1) Preliminary separation is unnecessary upon treatment with sulfuric acid and sulfur dioxide: 2) Moreover the complete and instantaneous precipitation of a minute quantity of thallium as $Co(NH_3)_6(TlCl_6)$ is made possible by the addition of ammonium chloride. Furthermore, this method is most remarkably accurate owing to its small factor of thallium as compared with any

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(5) R. Böttger, See foot-note (1); T. Carstanjen, See foot-note (1); T Carstanjen and Marquart, *Verh. Naturhist. Vereins. Reuss. Rheinlande Westfalens*, **24** (1867), *Correspondenzblatt* S **102**; D. Playfair, *Chem. N.*, **39** (1879), 245; A. V. Petar, See foot-note (1).

other factor used hitherto. For example, it is smaller than a half of the factor in the chromate method (0.77895) which had been hitherto the most widely used. Data concerning the locality of these samples and the occurrence of the ores used in these factories were destroyed during the war. Every effort was made since to obtain as full and as complete information as possible regarding these matters but with little success. Though it may not be perfect, an attempt is being made to revive the result obtained from the data.

(1) Thallium Content: The greater part of the samples analysed contained less than 0.05% for each, the total amounting to approximately 67%. Only three samples No. 7, No. 12, No. 13, are extraordinarily rich in thallium, but such a large amount as has been reported by former workers can not be found. No. 12 and No. 13 were chamber muds from pyrites burnt in a sulfuric acid factory. But the nature of the pyrites is not definite owing to data having been lost. The flue-dust used for sample No. 7 was sent from Saganoseki Refinery, one of the largest and oldest refineries in Japan, producing zinc and lead.

(2) Relation between thallium content and specific gravity: There are no samples whose specific gravity lies between 2.1 and 2.9. Therefore these samples can be divided into the two following groups according to specific gravity: Group A, less than 2.1 and Group B, larger than 3.0. The former occurs mostly in flue-dust and the latter, strictly in chamber muds from the sulfuric acid factory. The total content of thallium in almost all the samples, 62% of the whole, is each less than 0.05%. Samples with thallium content larger than 0.05 are as follows: Group A—No. 2, No. 7, No. 20, No. 29, No. 34; Group—B No. 1, No. 4, No. 11, No. 12, No. 13, No. 18, No. 21, No. 32, No. 36, No. 40, No. 42, No. 45, No. 48, No. 61.

Among these groups A and B, No. 7, No. 12, and No. 13 are remarkably abundant in thallium.

(3) Color and Thallium Content: A distinct relation between color and thallium content cannot be observed. However the color of a sample belonging to Group B is dull brown, sepia, chocolate tinged, while on the other hand Group A is dark olive, smoke grey tinged. Carstenjen had reported that red-tinged samples are richer in thallium than grey-tinged samples. Similar conditions may be said of this case also.

The author wishes to express his sincere appreciation to Prof. K. Kimura for his suggestion of the problem and his continued supervision through the investigation. He is also indebted to Miss F. Ueda who has kindly undertaken to perform a part of the experiment.

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