Radiometric Determination of Small Amounts of Thallium

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In 1940, a method of gravimetric determination of thallium which is based on the quantitative precipitation of thallium as $[Co(NH_3)_6](TlCl_6)$ was first reported by G. Spacu and A. Pope.(1) They determined about 100 mg. thallium by their method.

In 1949, examining this method carefully, Y. Murakami(2) improved it slightly and ascertained its excellent selectivity. According to this author an amount of thallium as small as 5 mg. could be determined precisely. In this paper, a new method of radiometric determination of smaller amounts of thallium, i. e. 3 mg. —0.5 microg. thallium is proposed.

This method consists in the precipitation of thallium by radioactive hexammine cobaltic trichloride which is labelled with cobalt-60 and the measurement of radioactivity of the precipitate which is due to the radioactive cobalt combined with hexachlorothallic ion as hexammine cobaltic ion. As the precipitation of thallium with hexammine cobaltic trichloride is highly selective, the method will be applied in various cases. However, the presence of radioactive thallium will disturb the determination. Therefore, for example, the determination of thallium contents in radioactive minerals will not be successful.

Further, it must be added that another method of radiometric determination of microamounts of thallium had been reported by H. Moureu et al.(3) in 1944. Their method is based on the formation of radioactive thallium iodide.

Experimental Part

(1) **Apparatus.**—Chemical procedures are operated in a microbeaker. For the filtration of the precipitate a filter-tube with a layer of sintered glass is used. The filtering surface is covered with fibres of filter paper, suspended in the water, by sucking up through the tube.

For the measurement of radioactivity, a Lauritsen electroscope made by the Scientific Research Institute, Tokyo, and a Geiger-Müller counter with a scaler of 32 which is prepared by Prof. T. Sasaki, Kyushu University, are used.

(2) **Reagents.** — Stock solution of thallium nitrate is prepared by dissolving thallous nitrate (Merck reagent), and standardised by the Spacu's method. Diluting this stock solution, a series of standard solutions (acidified slightly with nitric acid) is prepared.

Solution of potassium chlorate: 1 g. potassium chlorate is dissolved in 15 cc. distilled water.

Solution of hexammine cobaltic trichloride: According to the amounts of thallium to be determined, either the solution of the precipitant (A) or that of (B) is used.

Solution of the precipitant (A): 0.05 *M* aqueous solution of the hexammine cobaltic trichloride which is prepared by the Biltz's method(4) from 10 g. cobalt chloride containing about 2.5 mg. cobalt-60 chloride. This solution is used for the

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(1) G. Spacu und A. Pope, *Z. Anal. Chem.* **120**, 322 (1940).

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

(3) H. Moureu, P. Chovin and R. Daubel, *Chem. Abst.* **40**, 1752 (1946): *Compt. rend.* **219**, 127 (1944).

(4) H. Biltz, "Übungsbeispiel aus der anorg. Experimentalchemie", Leipzig, **1913**, s. 165.

determination of 3.1—0.034 mg. thallium.

Solution of the precipitant (B): About 0.05 *M* aqueous solution of the hexammine cobaltic trichloride which is prepared as above from 0.5g. cobalt chloride containing about 5 mg. cobalt-60 chloride. This solution is used for the determination of less than 30 microg. thallium.

(3) **Procedure.**—A known quantity of a thallium solution is taken from a burette into a microbeaker. 0.5 cc. of 1% ammonium chloride, 1—2 drops of hydrochloric acid (1:1) and 3—5 drops of potassium chlorate solution are added to the beaker. Thallium is oxidised to the thallic state by gentle boiling on a hot plate. When the volume of the liquid is reduced to less than one half, the beaker is removed from the hot plate and cooled on standing. The total volume of the solution must be 0.5—2 cc. Then 2—5 drops of the radioactive hexammine cobaltic trichloride reagent are added, until the solution is coloured orange red. If the amount of thallium present is less than about 30 microg., the precipitate is scarcely seen or is not seen at all. In such cases, it is preferable to leave it overnight. In other cases, the precipitate is formed immediately and it is necessary to leave it only for a short time. The precipitate formed as above is filtered with the above-mentioned filter-tube, and washed four times with small portions of 2% hydrochloric acid. Filtrate and washings are discarded. About 1 cc. of 3% hydrogen peroxide and a few drops of acetic acid are added to the beaker which contains the precipitate and filter-tube. After dissolving the precipitate by heating on a water bath, the solution is poured into a glass dish through the filtertube by suction. Several times the filter-tube and the inside of the beaker are rinsed with small portions of distilled water. All these washings are transferred into the glass dish. The combined solution in the glass dish is evaporated up on a water bath. After cooling, the radioactivity of the glass dish which contains the residue is measured.

(4) **Measurement of Radioactivity.**—Measured radioactivity of each specimen which is corrected for the natural leaks or natural counts is represented by divisions per minute (d/m), or counts per minute (c/m). The specimen obtained from 1.55 mg. Tl by using the solution of precipitant (A) is reserved as the standard of radioactive $[Co^*(NH_3)_6](TlCl_6)$. Shortly after the measurement of the radioactivity of each specimen, the radioactivity of the standard, $(d/m)_s$ or $(c/m)_s$ is measured in the condition of the same geometry. The ratio $(d/m)/(d/m)_s$ or $(c/m)/(c/m)_s$ is not affected by the variation of the sensitivity of the Lauritsen electroscope or the Geiger-Müller counter and the decay of the radioactivity of cobalt-60. So far as the reagent of the same bottle is used, the specific activity of the reagent is constant and the ratio $(d/m)/(d/m)_s$ or $(c/m)/(c/m)_s$ will depend only on the amount of thallium.

(5) **Results Obtained.**—The results for 3.1—0.034 mg. Tl are shown in Table 1. All these results are obtained by using the solution of the precipitant (A). From the Table 1 we can see that there are no serious differences between the results obtained by Geiger-Müller counter and those obtained by Lauritsen electroscope and that the relation between the amount of thallium and the ratio $(c/m)/(c/m)_s$ is almost linear. The deviations of $(c/m)/(c/m)_s$/mg. Tl of the each experiment from the mean value of $(c/m)/(c/m)_s$/mg. Tl, 0.701, are calculated in the fourth column, and from the mean value of the deviations we can estimate the accuracy of the determination.

Table 1

Results for 3.1—0.034 mg. Tl

mg. Tl (taken)	Measured by G. M. Counter $\frac{(c/m)}{(c/m)_s}$	Measured by G. M. Counter $\frac{(c/m)/(c/m)_s}{\text{mg. Tl}}$	% Deviation	Measured by Lauritsen Electroscope $\frac{(d/m)}{(d/m)_s}$
3.100	2.196	0.708	1.0	2.184
2.790	1.853	0.664	−5.3	1.857
2.325	1.534	0.659	−5.9	1.630
2.108	—	—	—	1.468
2.015	1.411	0.700	0.0	1.329
1.721	—	—	—	1.115
1.550	1.000	0.645	−8.0	1.000
1.225	0.871	0.711	1.4	0.867
0.744	0.493	0.662	−5.6	0.505
0.482	0.347	0.719	2.6	0.360
0.449	0.300	0.668	−4.7	0.303
0.360	0.273	0.755	7.7	0.259
0.228	0.171	0.750	7.0	0.163
0.130	0.098	0.753	7.4	0.096
0.077	0.064	0.831	18.5	0.059
0.034	0.020	0.588	−16.0	0.019
0.000	0.000	—	—	0.000
mean	—	0.701	±6.5	—

Table 2

Results for 24.6—0.46 microg Tl

microg Tl (taken)	$(d/m)/(d/m)_s$	$\frac{(d/m)/(d/m)_s}{\text{microg Tl}}$	% Deviation
24.6	0.619	0.0251	−14.4
23.4	0.657	0.0281	− 4.1
21.6	0.594	0.0275	− 6.1
18.4	0.517	0.0281	− 2.7
15.4	0.465	0.0302	3.1
12.9	0.370	0.0287	− 2.1
9.08	0.226	0.0248	−15.4
5.95	0.152	0.0255	−13.0
3.85	0.117	0.0303	3.4
1.86	0.063	0.0338	15.4
1.24	0.045	0.0363	23.8
0.46	0.015	0.0326	11.3
0.00	0.000	—	—
mean	—	0.0293	±9.5

If the amount of thallium is calculated from the following equation (1), the accuracy of the method will be in the order of $\pm(6-7)\%$.

$$\text{mg. Tl} = (c/m)/(c/m)_s/0.701 \qquad (1)$$

The results for 24.6−0.46 microg. Tl obtained by using the solution of the precipitant (B) are shown in Table 2. In these cases the radioactivity is measured only by the Lauritsen electroscope. From Table 2 we can see that the linear relation between the amount of thallium and ratio $(d/m)/(d/m)_s$ is not so good and that although more than about five micrograms thallium may be calculated from the following equation (2), it is preferable to use a working curve in the determination of thallium less than about five micrograms.

$$\text{microg. Tl} = (d/m)/(d/m)_s/0.029 \qquad (2)$$

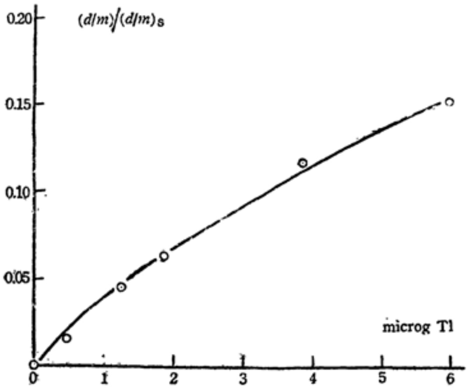

Fig. 1.—Working Curve for Determination of minute Amounts of Thallium

Fig. 1 shows the working curve for the determination of minute amounts of thallium. Roughly speaking, the error in the determination of the minute quantities of thallium is estimated about ten per cent or more.

(6) Application. — The method is applied to the determination of the thallium contents in volcanic rocks in the following procedure⁽⁵⁾:

To about 2 g. of finely divided rock powder in a platinum dish add about 8 cc. of 6N sulfuric acid and about 12 cc. of hydrofluoric acid. Evaporate to dryness and fume off the excess sulfuric acid avoiding decomposition of ferric sulfate. Take up the residue in a little water and again fume off the sulfuric acid. Treat the residue with water; warm to bring all soluble material into solution. Cool the solution and make up to about 100 ml. Reduce thallium to thallous state with hydroxylamine hydrochloride and add 5 cc. of 10% potassium cyanide and 5 cc. of 10% ammonium citrate. Adjust the *p*H to about 10 adding dilute ammonium hydroxide dropwise. Extract the mixture with four 10—15 cc. portions of 0.1% dithizone in chloroform. Combine the extracts and wash with 20—50 cc. of (1:1000) ammonium hydroxide. Separate the chloroform layer and shake the aqueous phase with a few cc. of dithizone solution to recover any thallium that may have passed into the ammonia solution. Shake the combined chloroform extracts with 10 cc. of (1:100) nitric acid and separate the chloroform layer. The aqueous layer is transferred to a microbeaker and evaporated to about 1 cc. or less. The resultant solution is treated as (3) using solution of precipitant (B).

To examine the recovery of thallium, known quantities of thallium standard solution are diluted to about 100 cc. and treated with dithizone following the above-mentioned procedure. Results are considerably low as shown in the Table 3.

Table 3
Recovery of Thallium

microg Tl (taken)	$(d/m)/(d/m)_s$	microg Tl (found) (a)	(b)	% Recovery
14.8	0.398	—	13.5	91
3.8	0.092	2.8	3.1	73—81

(a): calcd. from Fig. 1 (b): calcd. from Eq. (2)

Table 4
Thallium contents of Rocks

Sample	microg Tl (added)	$(d/m)/(d/m)_s$	microg Tl (found) (a)	(b)	%Tl
2.11 g. Liparite (Kozusima, Izu)	none	0.029	0.8	1.0	0.00005
2.04 g. 〃 (〃)	6.1	0.139	5.1	4.7	—
1.77 g. Basalt (Fuji)	none	0.003	0.1	—	0.00000

(a): calcd. from Fig. 1 (b): calcd. from Eq. (2)

The results obtained on two Japanese volcanic rocks are shown in Table 4. These values will be low from the above-mentioned results of examination of the extraction of thallium, but it will be sure that the thallium content of the liparite is in the order of $10^{-5}\%$.

Further study on the determination of thallium content of silicate rocks is to be continued.

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(5) c. f. F. J. Welcher, "Organic Analytical Reagents". Vol. 3, D. Van Nostrand Co, New York, (1949), p. 544.