

## Photometric Determination of Thallium with Rhodamine B

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(Received January 28, 1957)

In an earlier communication<sup>1)</sup> a photometric method for the determination of thallium with rhodamine B was briefly described. The purpose of the present paper is to treat the same subject in greater detail. The extraction with dithizone in chloroform was adopted for the separation of thallium from other elements. Although the recoveries of thallium are slightly low, the proposed method may be of general use for the determination of traces of this element.

### Experimental

**Apparatus.** Absorbance measurements were made with Hitachi Models EPB-U and EPV-2 spectrophotometers, using 1-cm. cells. At a later stage of the present investigation, the EPV-2 spectrophotometer was exclusively used.

**Solutions.** *Ammonium citrate*, 20 g. of  $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$  in 100 ml. of water.

*Potassium cyanide*, 10 g. in 100 ml. of water.

*Hydroxylamine hydrochloride*, 20 g. in 100 ml. of water.

*Dithizone*, 0.50 g. in 500 ml. of redistilled chloroform. Purify it freshly before use by washing the dithizone solution three times with 1:100 nitric acid, and then three times with 1:1000 ammonium hydroxide.

*Rhodamine B*, 0.20 g. in 100 ml. of water.

**Standard thallium solution.** Dissolve 0.124 g. of pure  $\text{Tl}_2\text{SO}_4$  in 100 ml. of 0.5 N sulfuric acid. From this stock solution (1.00 mg. Tl per ml.) prepare a working standard solution containing 0.010 mg. (10  $\mu\text{g.}$ ) of Tl per ml. by diluting with 0.5 N sulfuric acid. This solution can be kept for at least two weeks.

**Procedure.** Transfer the sample solution (1-10  $\mu\text{g.}$  Tl in a volume of about 30 ml.), which may conveniently be about 0.1 N in sulfuric acid, to a beaker and add 10 ml. of ammonium citrate solution. Add a few drops of thymol blue indicator solution and 1:1 ammonium hydroxide until the color turns blue. If, because of the presence of heavy metals, no color change can be definitely observed, adjust pH of the solution to 10 by the use of a pH meter.

Add 15 ml. of potassium cyanide solution and after a few minutes add 5 ml. of hydroxylamine hydrochloride and 3 ml. of 1:1 ammonium hydroxide, mix, and let stand for a few minutes.

If the color of the solution fades to a blue color, or nearly so, transfer the solution to a separatory funnel. If the deep red color produced does not fade appreciably upon standing for a few minutes, heat the solution on a water bath for 3-5 minutes, and then cool with water. Transfer the solution to a separatory funnel and wash the beaker with 10 ml. of 1:1000 ammonium hydroxide.

**Extraction of thallium.** Shake the solution for one minute with 10 ml. of dithizone solution. When the layers have separated, drain off the chloroform phase into another separatory funnel. Extract further the aqueous phase with two 10 ml. portions of dithizone solution. Combine the extracts and discard the aqueous layer. Wash the extracts with 10-20 ml. of 1:1000 ammonium hydroxide followed by 10-20 ml. of water. Drain the chloroform phase into another separatory funnel and shake vigorously for one minute with 10 ml. of 1:100 nitric acid to extract thallium. Draw off the chloroform into another separatory funnel and extract with another portion (5-10 ml.) of nitric acid. Drain off and discard the chloroform layer and transfer the aqueous extracts to a 50 ml. beaker containing 0.50 ml. of 1:5 sulfuric acid, rinse the separatory funnels with 1-2 ml. of 1:100 nitric acid and evaporate to fumes. When the sulfuric acid residue shows a brown color due to the presence of organic matter, add about 20 mg. of ammonium persulfate and allow to fume for a few minutes. Repeat this step until a colorless solution is obtained.

Cool, add 5.0 ml. of 2.0 N hydrochloric acid and 1.0 ml. of saturated bromine water. Heat near the boiling point and stop heating when the color due to bromine has disappeared. Cool to room temperature, transfer the solution to a 10 ml. volumetric flask and dilute to the mark with 2.0 N hydrochloric acid.

**Determination of thallium.** Transfer the solution to a separatory funnel as completely as possible, add 1.0 ml. of rhodamine B solution and mix. Without undue delay add 10.0 ml. of pure benzene and shake for one minute. When the two phases have separated, drain off the aqueous phase, transfer the benzene layer into a centrifuge tube, and centrifuge for about 2 minutes. Measure the absorbance of the clear benzene extract at 560 m $\mu$ , using benzene as the reference solution.

Establish the standard curve by taking, for example, 0, 2, 4, 7, and 10  $\mu\text{g.}$  of thallium into beakers respectively, adding 0.50 ml. of 1:5 sulfuric acid, 5.0 ml. of 2.0 N hydrochloric acid, 1.0 ml. of bromine water, and proceeding as described above. Run a blank through the entire procedure.

1) H. Onishi, This Bulletin, 29, 945 (1956).

As the recoveries of thallium are slightly low, a correction of +10 per cent. is probably advisable. See **Discussion**.

## Results and Discussion

**Photometric Determination of Thallium.** Bromine is a very satisfactory reagent to oxidize univalent thallium to tervalent. Excess of bromine can be easily removed by heating. The use of ammonium persulfate to destroy organic matter in the residue from the evaporation of nitric acid extract gave an opportunity to find another suitable oxidizing agent for thallium (Fig. 1). Oxidation with ammonium persulfate was effected in the following way. A known amount of thallium and 0.50 ml. of 1:5 sulfuric acid in a 50 ml. beaker were heated on a sand bath to fumes, about 20 mg. of ammonium persulfate was added and heated while whirling the beaker. After cooling

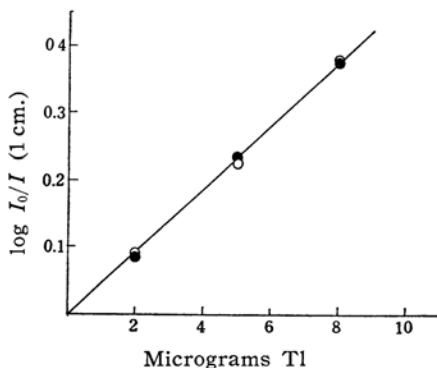


Fig. 1. Oxidation of thallium (I) with ammonium persulfate and bromine.

●: ammonium persulfate

○: bromine

1.6 N HCl, Hitachi EPV-2 spectrophotometer, 560 mμ.

the same amount of persulfate was again added and evaporated to fumes. A few drops of water were added and evaporated to fumes. Ten ml. of 2.0 N hydrochloric acid was added followed by rhodamine B-benzene extraction. When ammonium persulfate is left undecomposed and brought to rhodamine B extraction, rhodamine B is oxidized and erratic results are obtained. The above procedure eliminates this defect. However, that procedure appeared to be slightly more troublesome, so the step of bromine oxidation has been retained in the proposed procedure. Excess of persulfate was decomposed during the

treatment with bromine. Tervalent thallium obtained by either oxidation procedure was stable for at least one hour. Several other reagents were tried to oxidize thallium, but it was difficult to remove excess of any reagent without affecting the thallium. An attempt to remove the excess with an excess of rhodamine B was unsuccessful.

The absorptions spectrum (in benzene) of rhodamine B chlorothallate, which is considered to be the compound of thallium (III) with rhodamine B, is shown in Fig. 2. Correction is applied to the reagent blank. The absorption peak is found at

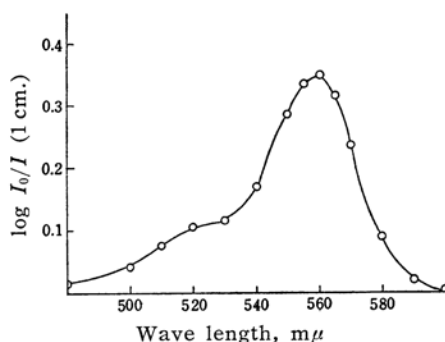


Fig. 2. Absorption spectrum of rhodamine B chlorothallate in benzene (0.8 p.p.m. Tl in benzene). Hitachi EPB-U spectrophotometer.

560 mμ. It is of interest to compare this peak with that of other compounds of the type (RH)M<sup>III</sup>Cl<sub>4</sub> (R=rhodamine B). Rhodamine B chloroantimonate, (RH)SbCl<sub>6</sub>, shows the maximum at 564 mμ, and rhodamine B chlorogallate at about 565 mμ<sup>2)</sup>. The maximum of RH<sup>+</sup> in water was found to be at 556 mμ<sup>3)</sup>. It does not seem that the absorption spectra of (RH)FeCl<sub>4</sub> and (RH)AuCl<sub>4</sub> have been described. At any rate, all three known compounds in benzene show the absorption peak at about 560 mμ. Moreover, the shapes of their absorption spectra are quite similar. The molar absorptivities of thallium, gallium, and antimony are 96,000\*, 60,000, and 100,000 respectively. The value for RH<sup>+</sup> in water is 110,000<sup>3)</sup>. It may be concluded that the deep coloration of these compounds is mainly due to RH<sup>+</sup> species.

The extractability of rhodamine B

2) H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, **13**, 159 (1955).

3) R. W. Ramette and E. B. Sandell, *J. Am. Chem. Soc.*, **78**, 4872 (1956).

\* A value of 87,000 was given in the previous paper. The EPB-U spectrophotometer gave low absorptivities.

chlorothallate as a function of hydrochloric acid concentration is shown in Fig. 3. The concentration was calculated and

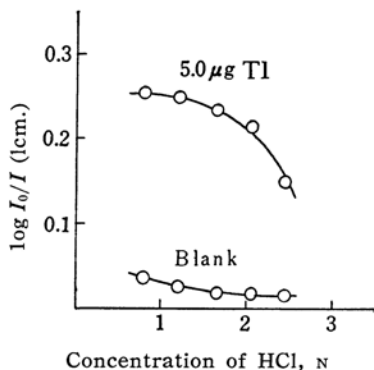


Fig. 3. Extractability of rhodamine B chlorothallate as a function of hydrochloric acid concentration. Hitachi EPV-2 spectrophotometer, 560 m $\mu$ .

correction was not made for evaporation loss during the treatment with bromine. A half ml. of 1:5 sulfuric acid was present in each case. In the figure 1.6N corresponds to the concentration of hydrochloric acid in the proposed procedure.

It is seen that the acid concentration must be kept constant to get reproducible results. Consequently heating in bromine treatment must always be done in the same way. At each hydrochloric acid concentration studied, i.e., 0.8, 1.2, 1.6, 2.0, and 2.5N, the absorbance was proportional to thallium concentration in the range 0.1 to at least 1 p.p.m. (based on the amount of thallium present originally in the aqueous phase).

The effect of the concentration of rhodamine B (reagent grade, Katayama Chemi-

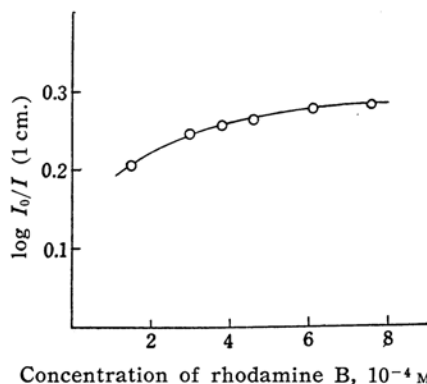


Fig. 4. Effect of rhodamine B concentration on absorbance of rhodamine B chlorothallate. 6.0  $\mu$ g. Tl taken, 2.0N HCl, Hitachi EPB-U spectrophotometer.

cal Works, Osaka) on the absorbance of rhodamine B chlorothallate in benzene is shown in Fig. 4. Corrections for reagent blanks were made. In all cases the hydrochloric acid concentration was maintained at 2.0N (slightly higher than the acidity recommended for **Procedure**). The absorbance increases very slightly with an increase in the concentration of rhodamine B, and the reagent blank also increases slightly. In the present investigation, about  $4 \times 10^{-4}$  M in rhodamine B (or 1.0 ml. of 0.20% rhodamine B solution) was adopted. At the concentration the reagent blank was in the range 0.010~0.020 against pure benzene. The extraction coefficient for 1.6N hydrochloric acid and 0.00038M rhodamine B in the aqueous phase is

$$\frac{[\text{Tl}]_{\text{benzene}}}{[\text{Tl}]_{\text{H}_2\text{O}}} = 13 \quad (\text{from Table 1})$$

This constant is independent of the thallium concentration in the range investigated. Consequently the volume of the aqueous phase must be maintained constant for reproducibility.

TABLE I  
EXTRACTABILITY OF RHODAMINE B CHLOROTHALLATE WITH BENZENE

[Aqueous phase (11 ml.) 1.6N in HCl and 0.00038 M in rhodamine B; 10 ml. benzene; temperature 18–20°C]

Tl present, $\mu$ g.	4.0	6.0	10.0
Absorbance of first extract (560 m $\mu$ )	0.175	0.262	0.435
Absorbance of second extract (10 ml.)	0.013	0.022	0.033
Extraction coefficient*	14.5	12	13.5

\* Average is 13.

The absorbance of the benzene extract does not change for at least one hour (Table II).

TABLE II  
STABILITY OF BENZENE EXTRACT

Time after extraction, min.	I	II	III
5	0.221	0.366	0.420
30	0.218	0.364	0.419
60	0.217	0.363	0.427

Most of the colorimetric methods available at the present time are indirect. The iodine method by Haddock<sup>4)</sup> was used for the determination of 10–200  $\mu$ g. of thallium after extraction with dithizone. Thallium

4) L. A. Haddock, *Analyst*, **60**, 394 (1935).

TABLE III

## DETERMINATION OF THALLIUM WITH RHODAMINE B AFTER DITHIZONE-CHLOROFORM EXTRACTION

Addition	Tl taken, $\mu\text{g.}$	Tl found, $\mu\text{g.}^*$		Tl recovered, %	
		Single $\text{HNO}_3$ extraction	Double $\text{HNO}_3$ extraction	Single $\text{HNO}_3$ extraction	Double $\text{HNO}_3$ extraction
none	2.2	1.9**, 2.1**		86**, 95**	
none	5.0	5.0**, 5.2**, 4.2, 4.5	4.5, 4.7	100**, 104**, 84, 90	90, 94
none	5.5	5.7**, 5.0**, 5.9**, 5.5**		104**, 91**, 107**, 100**	
none	8.7	7.8**, 7.8**		90**, 90**	
10 mg. Cu, 10 mg. Ni	5.0	4.6		92	
1.0 mg. Ag, 1.1 mg. Pt	5.0	4.2		84	
1.2 mg. Au(III), 1.0 mg. Sb(III)	5.0	4.9, 4.7		98, 94	
10 mg. Zn, 10 mg. Hg(II)	5.0		4.7		94
40 mg. Al, 1.1 mg. Ga	5.0	4.4		88	
1.1 mg. In	5.0		4.7		94
1.0 mg. Ge(IV), 1.0 mg. Sn(II)	5.0		4.6		92
1.0 mg. Pb	5.0		4.5		90
10 mg. P(as $\text{KH}_2\text{PO}_4$ ), 1.0 mg. As(III)	5.0		4.6		92
1.0 mg. Bi	5.0		4.6		92
1.0 mg. Mo(VI), 1.0 mg. W(VI)	5.0		4.4		88
50 mg. Fe(III)	5.0	4.2, 4.2		84, 84	
100 mg. Fe(III)	2.0	1.7		85	
100 mg. Fe(III)	5.0	4.3, 4.1	4.6, 4.5	86, 82	92, 90
100 mg. Fe(III)	8.0	6.6		83	

\* Correction applied for blank: 0.0  $\mu\text{g.}$  with no addition, and with Cu+Ni, Ge+Sn, Pb, P+As, Mo+W, and Fe; 0.1  $\mu\text{g.}$  with Au+Sb, Zn+Hg, and Al+Ga; 0.2  $\mu\text{g.}$  with Ag+Pt; 0.3  $\mu\text{g.}$  with In; and 0.4  $\mu\text{g.}$  with Bi.

\*\*  $\text{NH}_2\text{OH} \cdot \text{HCl}$  added before KCN, ammonium citrate, and  $\text{NH}_4\text{OH}$ .

dithizonate in chloroform was evaporated to dryness followed by oxidation with hydrogen peroxide.

Berg et al.<sup>5)</sup> described the determination with thionalide. Among the newer colorimetric methods, the *p*-phenetidine method<sup>6)</sup> has a sensitivity of about 0.3  $\mu\text{g. Tl/cm}^2$  corresponding to  $\log I_0/I=0.001$ , or a molar absorptivity of 6,000. Iron and gold interfere with the determination. Neither the dibenzylthiocarbamate<sup>7)</sup> nor thallium hydroxide<sup>8)</sup> methods are sensitive; the molar absorptivity of the former is 1,340 and that of the latter 561. Colorimetric determination of cobalt with nitroso-R salt after precipitation of  $[\text{Co}(\text{NH}_3)_6]\text{TiCl}_6$  gave the amount of thallium indirectly<sup>9)</sup>. This

precipitate was also utilized for the radio-metric determination of thallium by means of radioactive cobalt<sup>10,11)</sup>. This method and also the radioactivation method<sup>12)</sup> appear to be as sensitive as the rhodamine B method described here.

**Separation of Thallium.** Metals that must be separated because of more or less sensitive color reaction with rhodamine B are antimony, gold, iron, and tungsten. As much as 1 mg. of gallium in 2N hydrochloric acid does not give any appreciable color and does not interfere with the determination of thallium. As a method of separation of thallium, the extraction with dithizone is thought to be superior to the ether extraction of chloride or bromide. By the ether extraction gold will be extracted with thallium and it must be separated by an appropriate method, e.g., reduction to metal and filtration.

5) R. Berg, E. S. Fahrenkamp, and W. Roebeling, *Mikrochemie* (Molisch Festschrift), 42 (1936).

6) S. Iijima and Y. Kamemoto, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 75, 1294 (1954).

7) W. T. Foley and R. F. Pottier, *Anal. Chem.*, 28, 1101 (1956).

8) V. K. Zolotukhin and A. S. Molotkova, *Zhur. Anal. Khim.*, 11, 248 (1956).

9) T. Nozaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 77, 493 (1956).

10) T. Ishimori, *This Bulletin*, 26, 336 (1953).

11) T. Ishimori and Y. Takashima, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 76, 858 (1955).

12) C. J. Delbecq, L. E. Glendenin and P. H. Yuster, *Anal. Chem.*, 25, 350 (1953).

Dithizone extraction of thallium has been investigated by several workers. It is well known that the only metals reacting with dithizone in a slightly basic medium containing cyanide are bismuth, lead, thallium, and tin. Except thallium, none of these reacts with rhodamine B. Recently Ishimori<sup>10,11)</sup> determined traces of thallium radiochemically after its separation with dithizone. His results showed that the recoveries of thallium were 46 to 67 %, and the loss was found to occur when thallium was extracted with dilute nitric acid from dithizone-chloroform solution. Evaporation of dithizone-chloroform extract followed by oxidative decomposition of organic matter will undoubtedly bring better recoveries. This method is, however, not very convenient. In the present work, Ishimori's procedure was first re-examined. Thallium was reduced with hydroxylamine hydrochloride, and potassium cyanide and ammonium citrate were added. The pH of the solution was adjusted to about 10 by adding ammonium hydroxide. The dithizone extraction was then carried out. In the absence of foreign metals, the recoveries were satisfactory as shown by the results marked by \*\* in Table III. However, when the procedure was applied in the presence of iron(III), the recoveries of thallium became extremely low and yet the blank became higher. The present investigation has confirmed that the method of Sill and Peterson<sup>13)</sup> eliminated this difficulty.

Results obtained in applying the proposed method are collected in Table III. Most of the metals added were in the form of chloride, but some were sulfates or nitrates. It is seen that double nitric acid extraction is preferable to single extraction. In the presence of relatively large amounts of the metals reacting with dithizone, the extraction will have to be carried out more than three times. The recoveries of thallium were slightly low and it is believed that the application of a correction factor of +10 % is advisable. If the values in the table are increased by this amount, the recoveries become generally within 5 % of the theoretical values.

### Summary

Procedure is given for the spectrophotometric determination of 1-10  $\mu$ g. of thallium with rhodamine B. Ammonium persulfate was also found to be as effective as bromine in oxidizing thallium preparatory to rhodamine B-benzene extraction. For the separation of thallium from other elements, univalent thallium is extracted with dithizone in chloroform from a basic solution containing cyanide and then transferred to an aqueous solution by shaking the chloroform with dilute nitric acid. The procedure provides for the presence of antimony, gallium, gold, iron and tungsten.

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<sup>13)</sup> C. W. Sill and H. E. Peterson, *Anal. Chem.*, **21**, 1268 (1949).