Fluorometric Determination of Thallium with Rhodamine B

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After a study of a photometric (absorptiometric) determination of traces of thallium with rhodamine B[1,2], it was thought worthwhile to attempt a fluorometric determination of the element by making use of the same rhodamine B-benzene extraction technique. The orange-yellow fluorescence of the benzene extract of rhodamine B chlorothallate was already used by Feigl, Gentil, and Goldstein[3] for the detection of thallium.

Experimental

Apparatus. — A Hitachi EPV-2 spectrophotometer with a fluorescence attachment, type L-2, was used. It was equipped with a Toshiba SHL-100 UV lamp and a filter to transmit the 365 mμ mercury line. One-centimeter glass cells of which four sides are transparent, were used.

Solutions. — *Rhodamine B*, 0.0020% (W/V). This was chosen as a reference standard to adjust the instrument to a given sensitivity. Other solutions used were the same as described before[2].

Procedure.—The separation of thallium and the rhodamine B-benzene extraction were made essentially according to the directions previously described[2]. In establishing the standard curve, however, evaporation of standard thallium solution and 0.50 ml. of 1 : 5 sulfuric acid to fumes followed by the treatment with 5.0 ml. of 2.0 N hydrochloric acid and 1.0 ml. of saturated bromine water is recommended.

Measurement of the fluorescence intensity. Set the wave length scale at 580 mμ. For determining 1 to 10 μg. of thallium, set the sensitivity of the instrument at 10 (the highest sensitivity), and adjust the scale reading with 0.0020% rhodamine B solution to 100%. Measure the fluorescence intensity of the sample solution immediately.

Results and Discussion

The fluorescence spectra of aqueous rhodamine B solution[4] and rhodamine B chlorothallate in benzene are given in Figures 1 and 2. The fluorescence peaks of rhodamine B and rhodamine B chlorothallate are found at about 575 and 580 mμ respectively. As the slit widths used were large, these figures are somewhat approximate. However, the two curves are so similar that rhodamine B solution has been adopted as a reference standard to adjust the fluorometer scale. If total fluorescence measurements were made, other reference standards such as quinine sulfate could be used.

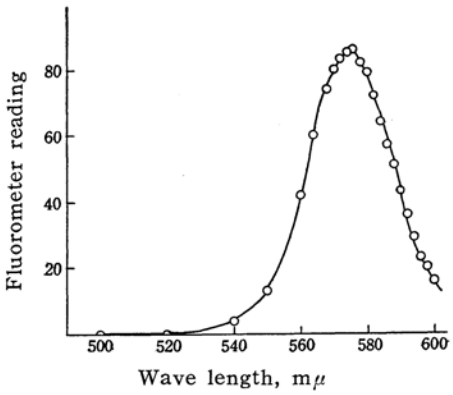

Fig. 1. Fluorescence spectrum of rhodamine B solution. 0.0020%, 1-cm. cell, slit width = 0.28 mm.

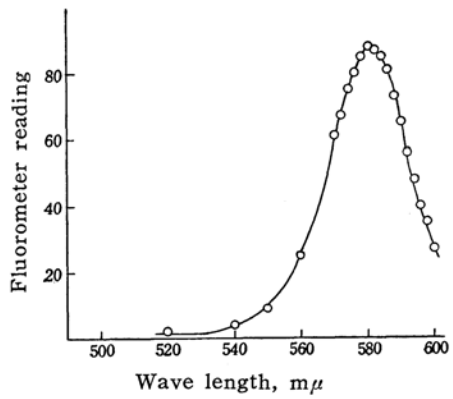

Fig. 2. Fluorescence spectrum of rhodamine B chlorothallate in benzene. 10 μg. Tl taken, 1-cm. cell, slit width = 0.36 mm.

In the present work, effects of variables such as the concentration of hydrochloric acid and rhodamine B were not particularly studied, and the conditions developed for the absorptiometry were accepted. A working curve is shown in Fig. 3. Curve

1) H. Onishi, This Bulletin, **29**, 945 (1956).
2) H. Onishi, This Bulletin, **30**, 567 (1957).
3) F. Feigl, V. Gentil, and D. Goldstein, *Anal. Chim. Acta*, **9**, 393 (1953).
4) For a more concentrated rhodamine B solution, see A. Murata and F. Yamauchi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **77**, 1259 (1956).

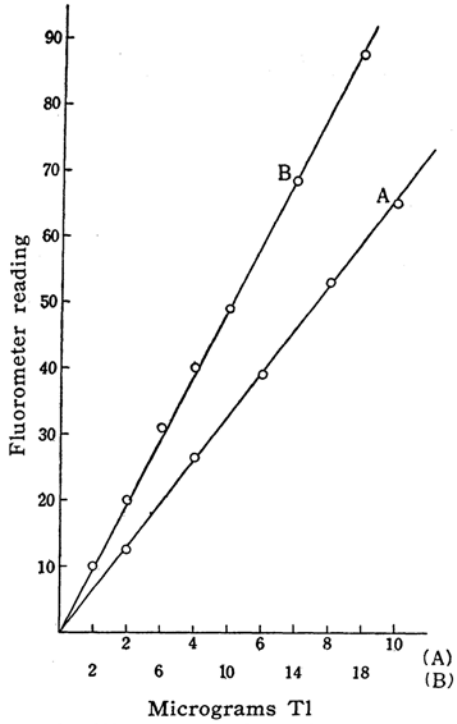

Fig. 3. Fluorescence intensity-concentration curve of thallium. Reference standard set at 100 for curve A, and at 70 for B, temperature 14—17°C.

A was obtained in setting the reference standard (0.0020% rhodamine B solution) at 100, whereas curve B was obtained at 70. It was observed that the fluorescence intensity of both rhodamine B solution and the benzene extract of rhodamine B chlorothallate decreased as the temperature was raised*. Consequently, working solutions as well as the sample should be at the same temperature. With the fluorometer used, the measurement of fluorescence intensity was made immediately after transferring the reference standard and the sample to the cell compartment. Fig. 3 shows that a satisfactory standard curve can be obtained by a careful and quick measurement. By decreasing the sensitivity and slit width of the instrument, larger amounts of thallium may be determinable. This point has not, however, been tested.

Effect of other elements on the photometric determination of thallium was previously described[2]. No serious interference was found by the elements studied. In fluorometry, it is not very uncommon that the presence of foreign substances sometimes interferes with the determination in a peculiar way, e.g., quenching. By carrying out the dithizone-chloroform extraction from basic solution containing cyanide, only lead, bismuth, and tin(II) are extracted with thallium (I). However, these elements in small quantities do not interfere with the fluorometric determination of thallium (Table I).

* With the instrument used (Hitachi EPV-2 with fluorescence attachment), the cell compartment was not well insulated from the heat of the light source.

TABLE I

DETERMINATION OF THALLIUM IN SYNTHETIC MAFIC ROCK*

Addition	Tl added, p.p.m.	Tl found, p.p.m.
none	none	0.15, 0.1
none	3.0	3.1, 2.6
0.1 mg. each Pb, Bi, Sn	none	0.1, 0.1
0.1 mg. each Pb, Bi, Sn	3.0	3.0, 2.8

* Percentage composition: 48 SiO_2, 12 Al_2O_3, 15 Fe_2O_3, 10 MgO, 10 CaO, 3 (Na_2O+K_2O), 1.5 TiO_2, 0.3 P_2O_5, 0.25 MnO.

A 1.0 g. sample simulating a mafic rock (10 per cent Fe) was decomposed with sulfuric- hydrofluoric acid, and the excess of sulfuric acid was driven off. The residue was taken up in water and the procedure for the dithizone extraction[2] was followed. Rhodamine B chlorothallate was extracted with 10 ml. of benzene after addition of 1 ml. of 0.20% (W/V) rhodamine B solution. In the table, +10% correction suggested previously, is not applied.

Although the present work has demonstrated the feasibility of a fluorometric determination of thallium, it does not appear that the method has any distinct advantages over the absorptiometric method. In sensitivity, the absorptiometric method is probably superior to the fluorometric. In accuracy, there may not be much difference between the two. The fluorometry is more susceptible to temperature.

Summary

A method is presented for the fluorometric determination of traces of thallium. Except for the step of fluorometry, the procedure is essentially the same as previously described for the absorptiometry. A synthetic mafic rock was analyzed for thallium by the method which involves hydrofluoric acid decomposition of the sample, dithizone extraction, rhodamine B-benzene extraction, and the measurement of fluorescence intensity on the benzene extract.

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