

## Extraction-Fluorimetric Determination of Microgram Amounts of Thallium with 2-Phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium Perchlorate

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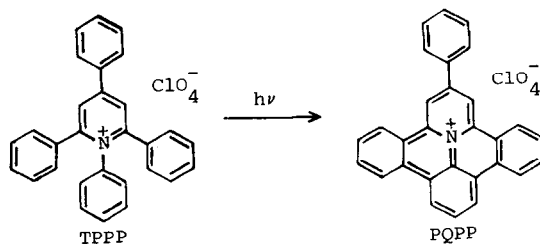
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In 0.5 *M* hydrochloric acid medium, thallium(III) forms with 2-phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium perchlorate (PQPP) an ion-association compound which is extractable in isoamyl acetate. The extracted ion-pair has a mole ratio Tl/PQPP in 1:1 and has been used for the spectrofluorimetric determination of thallium in the concentration range 0.06–1.6  $\mu\text{g}$  per 5 ml of organic layer. The interference of a large number of foreign ions has been investigated. The method is sensitive, accurate, precise, and specially useful for the determination of thallium in different materials with low contents of this element. © 1985 Academic Press, Inc.

### INTRODUCTION

Several fluorimetric methods are available for the determination of small amounts of thallium in solution; these utilize the violet fluorescence of the thallium(I) ion in the presence of excess chloride ion in concentrated hydrochloric acid (3, 9) and the reagents Rhodamine B, Acridine Orange, Acriflavine, and Rhodamine 6ZH have been used for the formation of ion-pair complexes with tetrachlorothalliate(III) which are extractable into an organic solvent for measurement of their fluorescence (2, 4, 5, 8, 10).

In a previous paper we introduced the reagent 2-phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium perchlorate for the fluorimetric determination of gold (7). This reagent is very simple to synthesize through a photochemical cyclization of 1,2,4,6-tetraphenylpyridinium perchlorate and besides, its multicyclic structure provides very good fluorescent characteristics.



PQP<sup>+</sup> forms ion-pair complexes with a small number of metal-halogen anions. These complexes may be used for the spectrofluorimetric determination of the metal after extraction with the appropriate organic solvent. Thallium(III) in dilute

hydrochloric acid forms an ion-pair complex with  $PQP^+$ , which is extracted into isoamyl acetate. The present paper describes the determination of microgram amounts of thallium with this reagent.

## MATERIALS AND METHODS

### *Apparatus*

Fluorescence spectra and spectrofluorimetric quantitative measurements were obtained with a Perkin–Elmer Model 3000 spectrofluorimeter equipped with a quantum counter; excitation spectra were corrected but emission spectra were not. A Perkin–Elmer Elemental Analyzer Model 240 B, a Perkin–Elmer 177 grating infrared spectrophotometer, a Hewlett–Packard 5980 A mass spectrophotometer, and a Varian FT-80 A nuclear magnetic resonance spectrometer were used for identification of the PQPP.

### *Reagents*

All solutions were prepared using analytical-grade chemicals and doubly distilled water.

*Synthesis of 2-phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium perchlorate.* 1,2,4,6-Tetraphenylpyridinium perchlorate (6) (0.5 g) dissolved in methanol (250 ml), was irradiated using an ultraviolet lamp, in a vessel equipped with an oxygen bubbler, for 3 hr. The precipitate was filtered-off and the filtrate was irradiated again to give second and third crops. The combined solids were recrystallized from methanol. Yield 70%; melting point 340°C. Elemental analysis: calcd C 72.5%; H 3.8%; N 2.9%; Found C 72.9%; H 3.8%; N 2.8%. The data obtained from the spectra of ir and NMR confirm the above structure.

*2-Phenylbenzo[8,9]quinolizino[4,5,6,7-fed]phenanthridinylium perchlorate solution,  $10^{-4}$  M.* This was prepared by dissolving 0.012 g of the reagent in ethanol. The solution is stable for several weeks.

*Thallium(III) standard solution 0.01 M.* Was prepared by dissolving thallium(III) chloride in 0.05 M hydrochloric acid and standardized by EDTA titration. Working standards were prepared from this solution as required.

### *Procedures*

*Determination of thallium(III).* Place a volume of sample solution containing 0.06–1.6  $\mu\text{g}$  of thallium in a separatory funnel. Add 5 ml of 5 M hydrochloric acid and 2 ml of  $7 \times 10^{-5}$  M PQPP solution. Dilute the volume to 50 ml with doubly distilled water. Shake with 5 ml of isoamyl acetate for 1 min and allow the phases to separate for 5 min and then transfer the organic layer into a centrifuge tube, and centrifuge it to give an organic layer free from water. Activate at 300 nm and read the fluorescence of the complex at 461 nm. Calculate the thallium concentration from a previously prepared calibration graph.

*Determination of thallium in leads.* The samples were dissolved in nitric acid and boiled to near dryness twice with doubly distilled water to reduce the acidity. Dissolve the residue in doubly distilled water and add 1 ml of bromine water. Heat to drive off the bromine and then cool. The thallium was determined in such solutions by the recommended procedure.

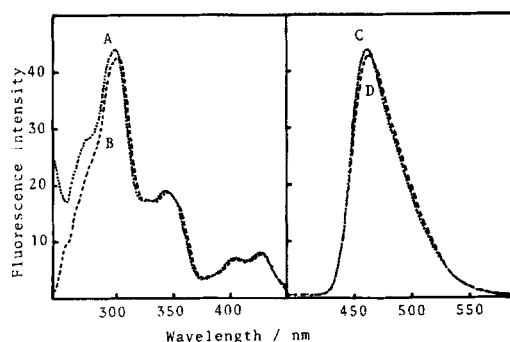


FIG. 1. Excitation and emission spectra: (A) and (C) reagent in ethanol; (B) and (D) thallium complex,  $\text{PQP}^+ \text{TiCl}_4^-$ , in isoamyl acetate.

To avoid the interference of such high concentration of  $\text{Pb(II)}$  prepare a calibration graph using a similar concentration of lead as in the sample solution. The results are shown in Table 2.

## RESULTS AND DISCUSSION

### Fluorescence Spectra

The excitation and emission spectra of the reagent (in ethanol) and the  $\text{PQP}^+ \text{TiCl}_4^-$  (in isoamyl acetate) are shown in Fig. 1. The excitation spectra have maxima at 300, 346, and 428, nm and the emission spectra have a maximum at 461 nm. The fluorescence quantum efficiency of PQPP ( $\lambda_{\text{ex}} = 300$  nm) in ethanol was determined by the Gains and Dawson method (1) and a value of 0.59 was obtained.

### Effect of Hydrochloric Acid Concentration

The effect of the concentration of hydrochloric acid on the formation of the  $\text{PQP}^+ \text{TiCl}_4^-$  complex and its extraction into isoamyl acetate was studied using fixed concentrations of thallium(III) (13 ppb) and PQPP ( $8.2 \times 10^{-7}$  M) and varying the hydrochloric acid concentration from 0.01 to 2 M. The fluorescence intensity remained constant between 0.5 and 1 M in hydrochloric acid.

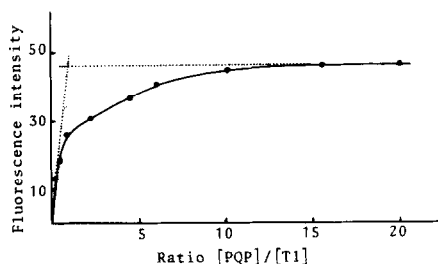


FIG. 2. Stoichiometry of thallium-PQPP complex determined by the molar-ratio method; thallium(III) concentration  $9.73 \times 10^{-8}$  M.

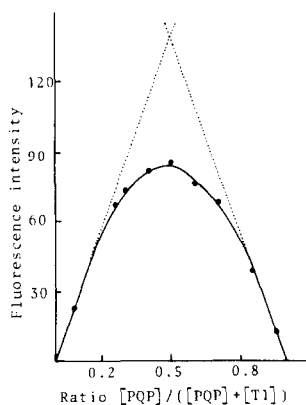


FIG. 3. Stoichiometry of thallium-PQPP complex determined by Job's method; concentration of thallium(III) plus ligand  $5 \times 10^{-7} M$ .

### Composition of the Complex

To establish the composition of the complex, the continuous variations and molar ratio methods were applied in 0.5 *M* hydrochloric acid. The mole ratio of thallium to PQPP was found to be 1:1 by two methods (Figs. 2 and 3). Figure 2 shows that a molar ratio  $[PQPP]/[Tl(III)]$  higher than 14 is necessary for the complete formation and extraction of the complex. The apparent stability constant of the complex was calculated from the results of the molar ratio and Job's methods, and an average value of  $\log K = 6.3 \pm 0.1$  at 20°C was obtained.

### Extraction Efficiency and Stability

The ratio by volume of aqueous phase to isoamyl acetate selected was 10 at 1. The extraction efficiency was 94%. The fluorescence intensity values of the complex extracted in isoamyl acetate remain constant at least 30 min.

TABLE I  
Effect of Diverse Ions on the Determination of 0.8  $\mu g$  of Thallium

Tolerance ratio [Ion]/[Tl(III)]	Ion added
0.05	Au(III)
0.2	Hg(II)
1	Fe(III), Pt(IV)
10	Bi(III), Pd(II), As(V)
20	Sb(V)
200	Mo(VI)
500	In(III), Cr(III), Mn(II), Cu(II), Zn(II)
1,000	Ga(III), $ClO_4^-$
5,000	Ag(I), Pb(II)
10,000	$PO_4H_2^-$
50,000	Cd(II)
$10^6$	$SO_4^{2-}$
$2 \times 10^6$	$NO_3^-$

TABLE 2  
Determination of Thallium in a Lead Sample<sup>a</sup>

Composition of sample (%)		Tl (%)	
		Present	Found
Pb 99.996	Te 0.0005	0.001	0.0008
Cu 0.0006	Al 0.001		
Ag 0.0001	Cd 0.0001		
Bi 0.0008			

<sup>a</sup> Certified by British Chemical Standards.

### Calibration Graphs

Under the recommended conditions in the procedure, the calibration graph was linear over the concentration range 1.2–32 ppb. The coefficient of variation obtained from 10 measurements of 25 and 10 ppb of thallium(III) was  $\pm 2.3$  and 1.6, respectively.

### Effect of Other Ions

For the determination of 16 ppb of thallium(III) by this method, extraneous ions can be tolerated at the levels given in Table 1. The limiting value of the concentration of foreign ion was taken as that value which caused an error of not more than 4% in the fluorescence intensity values. Anions were added as chlorides, nitrates, or sulfates, and cations in the form of sodium or potassium salts.

The positive interference can be attributed to the fact that those elements also form ion-pair compounds with the reagent in hydrochloric acid and so are slightly extracted into the organic solvent. Gold, mercury, platinum, and iron cause serious interference.

### Applications

The method was checked for its application to the determination of thallium in leads with very low contents of thallium. The results are shown in Table 2.

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