

SHORT COMMUNICATIONS

INDIRECT DETERMINATION OF THALLIUM BY DIFFERENTIAL-PULSE POLAROGRAPHY*

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Summary—The method is based on the separation of Tl(I) as $Tl_2HPMo_{12}O_{40}$, stripping of the molybdate, and measurement of the peak current in differential-pulse polarography of the molybdenum. The calibration graph is linear over the range 2–12 ppm of thallium. The relative standard deviation is 1.2% (7 replicates each containing 500 μ g of thallium). The current due to reduction of the molybdenum is three times that for reduction of the equivalent amount of Tl(I) in the thallos phosphomolybdate precipitate, making the indirect approach more sensitive than direct polarographic determination of the Tl(I).

The development of new methods for determination of thallium is of importance because of the toxicity of the element.¹ The polarographic behaviour of thallium in pyridine and in different buffer solutions and supporting electrolytes has long been investigated.²⁻⁵ The determination of thallium by d.c. polarography in succinic acid medium has been reported.⁶ Thallium has been determined in the presence of large amounts of copper and cadmium by means of the effect of the adsorption of camphor on the DME.⁷ Other methods used include a.c. polarography, stripping analysis and differential pulse polarography.⁸⁻¹¹

The present work deals with indirect determination of thallium by differential-pulse polarography. Tl(I) is separated as the phosphomolybdate and the molybdenum and Tl(I) in the precipitate are determined polarographically. The ratio of molybdenum to thallium in the precipitate has been shown to be 6:1.¹²

EXPERIMENTAL

Chemicals

Stock thallium solution (1 mg/ml). Dissolve 1.304 g of pure $TlNO_3$ in distilled water and dilute to the mark in a 1-litre standard flask. Transfer to a polyethylene bottle.

Standard thallium solution (100 μ g/ml). Transfer 50 ml of the stock solution to a 500-ml standard flask and dilute to the mark with distilled water. Store in a polyethylene bottle.

Basic borate buffer. Transfer 15 ml of 50% sodium hydroxide solution to a 1-litre flask. Add about 300 ml of distilled water and 48.0 g of boric acid. Swirl to dissolve and dilute to the mark with distilled water. Store in a polyethylene bottle. The pH of this solution is 8.9.

Perchloric acid, 0.5M. Add 43 ml of concentrated (72%) perchloric acid to about 200 ml of distilled water, cool and dilute to 1 litre. Store in a polyethylene bottle.

Perchloric acid, 4.0M. Add 86 ml of concentrated (72%)

perchloric acid to about 100 ml of distilled water, cool and dilute to 250 ml. Store in a polyethylene bottle.

Phosphomolybdic acid solution, 10%. Dissolve 10 g of phosphomolybdic acid in 100 ml of water. Filter the solution through a fine-porosity sintered-glass crucible and transfer into a polyethylene bottle.

Apparatus

Differential-pulse polarograms were obtained with an EG&G PAR 174 Polarographic Analyzer equipped with a model 303 static mercury-drop electrode and a Houston model RE0089 X-Y recorder.

Procedure

Transfer a sample containing between 100 and 600 μ g of thallium(I) into a 30-ml centrifuge tube, acidify with 2.0 ml of 4.0M perchloric acid and dilute to 10 ml with distilled water. Add 5.0 ml of 10% phosphomolybdic acid solution and wait for 10 min for complete formation of the thallos phosphomolybdate precipitate.

Centrifuge for 10 min at about 16,000 rpm. Remove and discard the supernatant liquid. Wash the precipitate with 10.0 ml of 0.5M perchloric acid, being sure to start washing at the top of the tube and work down to ensure removal of any phosphomolybdic acid adhering to the sides of the tube. Centrifuge for 5 min, then remove and discard the wash solution. Add 25 ml of the borate buffer to the precipitate, directing the stream of the buffer at the precipitate, and wait for dissolution to become complete. Transfer the solution to a polyethylene beaker containing 0.62 g of citric acid monohydrate, and rinse the tube with distilled water into the beaker. Rinse the tube again, with 5 ml of borate buffer, and transfer the washings to the beaker. Transfer the contents of the beaker to a 50-ml standard flask, dilute to the mark with distilled water, and mix.

Transfer a portion of the solution into a polarographic cell and record the differential-pulse polarogram, scanning from -0.2 to -1.5 V vs. Ag/AgCl, at 5 mV/sec, using a modulation amplitude of 50 mV, with medium drop-size, a drop-time of 0.5 sec, and a purge time of 4 min.

RESULTS AND DISCUSSION

The effect of the acidity used in precipitation of $Tl_2HPMo_{12}O_{40}$ was studied with samples containing 400 μ g of Tl(I). Table 1 shows that between 1.0 and

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Table 1. Effect of acidity on the formation of $Tl_2HPMo_{12}O_{40}$ [400 μg of Tl(I), scan-rate 2 mV/sec, drop time 1.0 sec, modulation amplitude 50 mV]

| 4.0M $HClO_4$ added, ml | i_p (*), μA | |
|----------------------------|--------------------------|---------------------|
| | Direct, Tl(I) | Indirect, molybdate |
| 0.5 | 1.89 | 4.18 |
| 1.0 | 1.93 | 4.45 |
| 1.5 | 1.90 | 4.35 |
| 2.0 | 1.93 | 4.45 |

*Mean of three values.

2.0 ml of 4.0M perchloric acid can be used; 2.0 ml was chosen for the recommended procedure.

The voltage at which the peak of Tl(I) appears in the polarogram is rather insensitive to pH, and is about -0.4 V (vs. Ag/AgCl) at both pH 8.8 and 6.1. If the precipitate is decomposed in the pH-8.78 borate buffer without addition of citric acid, only Tl(I) is reduced, at -0.4 V (Fig. 1). If the acidity is adjusted with 0.62 g of citric acid monohydrate, both Tl(I) and the released molybdate are reduced, with good resolution between the two peaks. The pH of the resulting solution is 6.07, and this was chosen as the optimum pH. At a much lower pH the resolution is not

adequate. The addition of the buffer serves two purposes: the first is to dissolve the precipitate, and the second to decompose the phosphomolybdate. The addition of citric acid also serves two purposes: the first is to adjust the pH, and the second to complex the molybdate to prevent re-formation of phosphomolybdate. For seven replicate determinations of 500 μg of thallium(I) by the procedure given, the thallium(I) peak gave $E_p -0.413 \pm 0.002\text{ V}$, i_p 2.29–2.43 μA , and the molybdate peak gave $E_p -1.245 \pm 0.005\text{ V}$, i_p 7.04–7.32 μA .

A typical differential-pulse polarogram at pH 6.1 is shown in Fig. 2. It exhibits two peaks, the first (at -0.4 V) due to reduction of Tl(I) and the second (at -1.2 V) due to reduction of the molybdate. Thus, the heights of the two peaks can be used for the simultaneous direct and indirect determination of thallium with the one polarogram.

The precision was estimated by analysing seven samples each containing 500 μg of thallium. The average current for the thallium peak was 2.33 μA and the relative standard deviation 2.6%, and the average current for the molybdate peak was 7.19 μA , relative standard deviation 1.2%. Hence mea-

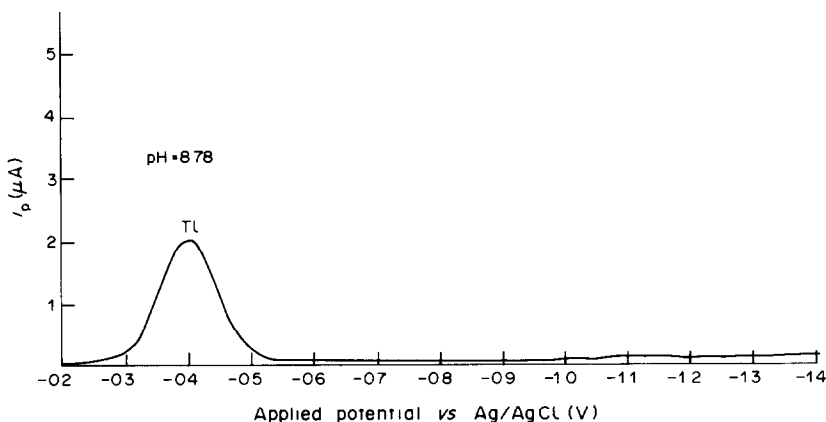


Fig. 1. A differential pulse polarogram of a sample containing 400 μg of Tl(I), pH = 8.78, without citric acid addition. Drop time = 1.0 sec. Scan-rate = 2 mV/sec.

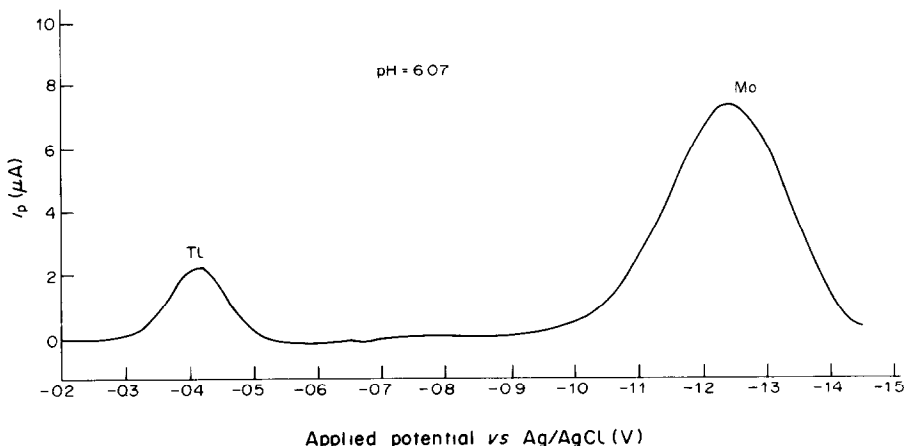


Fig. 2. A typical differential pulse polarogram of a sample containing 500 μg of Tl(I) at pH = 6.07, with citric acid addition.

Table 2. Effect of the presence of foreign ions on determination of 400 μg of Tl(I)

| Ion | Added as* | Amount of ion added, μg | Tl peak | | Mo peak | |
|---------------------|---|------------------------------------|-------------------------|--------|-------------------------|--------|
| | | | Current†, μA | RE,§ % | Current†, μA | RE,§ % |
| Ag^+ | AgNO_3 | 100 | 1.90 | +2.2 | 5.50 | -1.3 |
| Ag^+ | AgNO_3 | 200 | 1.88 | +1.1 | 5.52 | -0.9 |
| Ag^+ | AgNO_3 | 400 | 1.88 | +1.1 | 5.67 | +1.8 |
| Pb^{2+} | PbNO_3 | 400 | 1.83 | -1.6 | 5.43 | -2.5 |
| Cd^{2+} | CdCl_2 | 100 | 1.85 | -0.5 | 5.53 | -0.7 |
| Cd^{2+} | CdCl_2 | 200 | 1.88 | +1.1 | 5.58 | +0.2 |
| Cd^{2+} | CdCl_2 | 400 | 1.87 | -0.5 | 5.60 | +0.5 |
| Ba^{2+} | $\text{Ba}(\text{NO}_3)_2$ | 400 | 1.84 | -1.1 | 5.48 | -1.6 |
| CrO_4^{2-} | K_2CrO_4 | 400 | 1.83 | -1.6 | 5.52 | -0.9 |
| WO_4^{2-} | $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ | 400 | 1.83 | -1.6 | 5.45 | -2.2 |
| Cu^{2+} | $\text{Cu}(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ | 400 | 1.79 | -3.8 | 5.46 | -2.0 |
| Hg^{2+} | $\text{Hg}(\text{NO}_3)_2$ | 400 | 1.80 | -3.2 | 5.52 | -0.9 |
| Ni^{2+} | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ | 400 | 1.87 | +0.5 | 5.53 | -0.7 |
| Fe^{3+} | $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 400 | 1.85 | -0.5 | 5.48 | -1.6 |
| NH_4^+ | NH_4Cl | 100 | 1.88 | +1.1 | 5.67 | +1.8 |
| NH_4^+ | NH_4Cl | 200 | 1.85 | -0.5 | 5.88 | +5.6 |
| NH_4^+ | NH_4Cl | 400 | 1.85 | -0.5 | 6.13 | +10.1 |

*Solutions were made in distilled water, except for $\text{Hg}(\text{NO}_3)_2$, which was dissolved in 0.032M HNO_3 .

†Each value is the average from three separate samples.

§The relative error (RE) is calculated relative to 1.86 μA for the Tl current and 5.57 μA for the Mo current.

surement of thallium by means of the molybdate peak is more sensitive and precise.

Calibration graphs with good linearity are obtained for thallium in the range 2–12 $\mu\text{g}/\text{ml}$ in the final 50 ml of solution, for both the thallium and molybdate measurements, the slope of the "molybdate" plot being about 3 times that of the "thallium" plot. Both plots give an intercept on the concentration axis at about 0.7 $\mu\text{g}/\text{ml}$ thallium concentration, which implies a solubility of about $6 \times 10^{-6}M$ for $\text{Tl}_2\text{HPMo}_{12}\text{O}_{40}$ at the acidity used for the precipitation.

A study was made of the degree of interference by 100–400 μg amounts of various ions at the 400- μg Tl(I) level. Table 2 summarizes the results. The only significant interference is from the ammonium ion when present in amounts above about 100 μg , but even then only for the indirect determination, since it is due to precipitation of ammonium phosphomolybdate, which naturally results in a higher molybdate peak. The direct method is applicable in the presence of at least 400 μg of ammonium ion. Although thallos chromate is only sparingly soluble, its precipitation is prevented by the acidification of the sample with perchloric acid, because of conversion of the chromate into dichromate. Organic bases, rubidium and caesium were not tested, but would be expected to interfere in the indirect (but not the direct) determination because they form insoluble phosphomolybdate salts in acidic medium.^{13–15}

The final test solution is fairly stable and there is a change of only +1.1% in peak current if the

solution is kept for 24 or 48 hr before the direct measurement, and +1.3% (24-hr storage) and +2.2% (48-hr storage) in the peak current for the indirect measurement, for thallium at the 400- μg level (mean of three replicates).

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