TRACE DETERMINATION OF THALLIUM BY DPP AND DPASV

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Thallium is one of the highly toxic metals [1] with low natural abudance. A wide range of techniques have been used for its analysis e.g. gas-liquid chromatography [2], colorimetry [3], mass-spectrometry [4], atomic absorpiton spectroscopy [5,6] alternating current voltammetry [7,8], square wave polarography [9], cathode ray polarography [10], differential pulse polarography [11] and some stripping voltammetric procedures [12].

This communication describes both differential pulse polarographic and anodic stripping procedure for trace determination of thallium (I).

EXPERIMENTAL

The investigations were carried out in a Metrohm-E-506-Polarecord. Working electrode was either a DME or a HMDE (Metrohm-Kemula type), reference electrode was a Ag/AgCl (satd. KCl) while .Pt wire served as an auxiliary electrode.

Reagents

All chemicals used were of AR grade. Triple distilled water was used throughout the present work. A 4000 ppm stock solution of Tl (I) was prepared by dissolving calculated amount of TlCl (AR, BDH) in water acidified with a few drops of conc. H_2SO_4. Working standards (2000 µg/ml for DPP and 5 µg/ml for DPASV) were prepared by suitable dilution with water. Stock solutions (0.1M) of different cations were prepared and dilutions were made as necessary.

Procedure

2.5 ml of 1.0 M tartaric acid and 5.0 ml of 0.5 M disodium tartrate solutions were mixed and diluted to 25 ml. To this,25 ul of Tl(I) solution 2000 µg/ml) was added. The solution was maintained at $25^{\circ} \pm 0.5^{\circ}$C and was deaerated with nitrogen for 10 minutes and DPP was recorded keeping the pulse amplitude of 2,20 and 40 mV, drop time of 1 sec and scanning the potential in the range -0.2 to-1.5 V at a rate of 6 mV/sec.

For DPASV studies, 5.0 ml of 0.05 M KNO_3 solution was diluted to 25 ml, to it was added 25 µl of Tl(I) solution (5 µg/ml) and nitrogen gas was passed to make it oxygen free. Electrolysed at -0.6 V for 1 min and scanned in the range -0.6 V to 0 V at a scan rate of 4 mV/sec.

RESULTS AND DISCUSSION

Differential Pulse Polarography of Thallium(I)

Effect of Supporting Electrolyte

In the present studies, eighteen different electrolytes namely; HCl , HNO_3 , $HClO_4$, KNO_3 and KCl each at 1.0 M and 0.5 M concentrations, 0.5 M citric acid with 0.5 M trisodium citrate, salicylic acid (0.1 M) with sodium salicylate (0.1 M) succinic acid 0.01 M, 0.1 M succinic acid with 0.1 M sodium succinate, satd. malonic acid, pyridine 0.5 M + KCl 0.5 M, triethanolamine 0.3 M with KOH 0.1 M, oxalic acid 0.01 M, KCl 0.5 M with HCl 0.5 M; and varying concentrations of tartaric acid with disodium tartrate i.e. 0.1 M each, 0.25 M each, and 0.01 M each; were studied as supporting electrolytes for Tl(I) determination.

The Tl(I) reduction peak occurs at $E_p \simeq 0.45$ V vs. Ag/AgCl electrode, in most of the media studied. In KCl (0.5 M) with HCl (0.5 M) mixture the reduction peak occured at $E_p = \simeq 0.476$ V. In 0.1 M succinic acid + 0.1 M sodium succinate medium, no identifiable response for Tl(I) reduction has been observed.

The reduction signal obtained in almost all the media studied was in the form of a broad symmetric peak of an average peak half width of 20 mV. Two media, namely, HCl (1.0 M) and tartaric acid (0.1 M) + disodium tartrate (0.1 M) mixture, exhibited higher I_p values (9 nAmp) as compared to the other media studied (4 to 5 nAmps) for Tl(I) concentration of 2 ppm. However, the occurrence of hydrogen evolution beyond potential of -0.9 V restricted the effective scan range in HCl (1.0 M) medium, while no such phenomenon is observed in tartaric acid 0.1 M + disodium tartrate 0.1 M mixture.

Tl(I) undergoes reversible reduction in tartaric acid + disodium tartrate medium yielding a peak at -0.446 V vs Ag/AgCl reference electrode. All further DPP studies

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in the present work have been carried out in this buffer.

Calibration Plots

A set of three linear calibration plots in the range of 1.0 to 10.0 ppm, 0.1 to 1.0 ppm and 20 ppb to 100 ppb of Tl(I) has been obtained. The minimum detection limit and relative mean deviation is found to be 20 ppb and ±1.6% respectively.

Interference Study

The determination procedure is fairly selective towards the presence of other ions except for Tl(III) and Pb(II), which seriously interfere in the determination. The tolerance limits for Cu(II), Cd(II), Ni(II), As(III), Fe(III), Zn(II), Bi(III) and Cr(III) ions are 1:50, 1:20, 1:1000, 1:30, 1:200, 1:1000, 1:50, and 1:50, respectively.

TABLE 1

Effect of Supporting Electrolytes in DPASV Determination of Tl(I).

Tl(I) = 5 ppb, Electrolysis potential = -0.6 V, Enrichment time = 1 min, Quiescent time = 10 sec, Electrode surface area = 2.20 mm^2.

Supporting Electrolyte	E_p(Volts)	I(nA)
0.1 M tartaric acid	-0.430	ill defined peak
0.01 M tartaric acid	-0.430	ill defined peak
0.1 M succinic acid	-0.430	ill defined peak
0.01 M salicylic acid	-0.436	16
0.01 M KCl	-	ill defined peak
0.01 M HCl	-0.428	25
0.1 M HCl	-0.428	ill defined peak
0.1 M H_2SO_4	-0.436	25
0.01 M H_2SO_4	-0.436	ill defined peak
0.01 M HNO_3	-0.432	19
0.1 M HNO_3	-0.440	23
0.1 M $HClO_4$	-0.436	25
0.1 M NaOH	-0.432	17
0.01 M NaOH	-0.432	26
0.1 M NH_4OH	-0.424	27
0.01 M NH_4OH	-0.428	27
0.05 M KNO_3	-0.440	27
0.1 M KNO_3	-0.436	25
0.01 M KNO_3	-0.432	27
0.1 M CH_3COOH	-0.426	17
0.01 M CH_3COOH	-0.420	15
0.01 M Oxalic acid	-0.380	ill defined peak

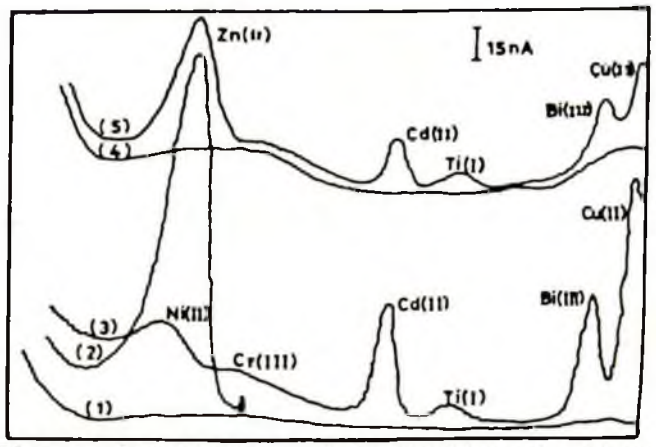


Fig. 1 Simultaneous determination of cations in 0.1 M tartaric acid +0.1 M disodium tartrate supporting electrolyte by differential pulse polarography.

Curve 1,2,3 pulse amplitude 4 mV
Curve 4,5 pulse amplitude 20 mV
1 and 4 blank
2 Zn 6 ppm; Tl(I) 2 ppm; Cd 4 ppm; Cu 5 ppm; Bi 5 ppm;
3 Cu 5 ppm; Bi 5 ppm; Tl 2 ppm; Cd 4 ppm; Cr 4 ppm; Ni 10 ppm;
5 Cu 0.5 ppm; Bi 0.5 ppm; Tl(I) 0.4 ppm; Cd 0.4 ppm; Zn 1 ppm.

Simultaneous Determination

It is possible to determine, Cu(II), Bi(III), Tl(I), Cd(II), Cr(III), and Zn(II)/Ni(II) simultaneously. These ions exhibit a DP peak in the tartaric acid (0.1 M) + disodium tartrate (0.1 M) supporting medium at potentials -0.03 V, -0.096 V, -0.446 V, -0.590 V, -0.868 V, -1.022 V and -1.076 V corresponding to Cu(II), Bi(III), Tl(I), Cd(II), Cr(III), Zn(II) and Ni(II) respectively. A set of two such representative polarograms with their respective blanks are shown in Fig. 1.

Seperate calibration plots of Tl(I) in 2-10 ppm range in presence of each of these cations were obtained and found to be linear. The Cu(II) and Bi(III) peaks are not far apart and hence a 1:1 ratio of Cu:Bi is necessary for effecting their precise and meaningful simultaneous determination.

Differential Pulse Anodic Stripping Voltammetry of Thallium (I)

Effect of Supporting Electrolyte

All preliminary DPASV studies have been

performed at Tl(I) concentration of 5 ppb.

A set of eleven different electrolytes, each at 0.1 and 0.01 M concentrations were studied as supporting electrolytes for Tl(I) determination by DPASV in the present studies (Table 1). The recording conditions being maintained as mentioned earlier.

The anodic dissolution peak in 0.01 M KNO_3 medium occurs at -0.432 V vs Ag/AgCl reference electrode and is chosen as the analytical peak in the present studies.

All DPASV experiments in the present studies have been carried out with electrolysis potential of -0.6 V.

Enrichment time of 1 minute and quiescent time of 10 sec has been used throughout the studies except the calibration curve range of 0.1 to 1.0 ppb Tl(I) where the enrichment and quiescent time periods were 10 minutes and 30 seconds, respectively.

HMDE with surface area of 2.20 mm^2 has been used uniformly.

Calibration Plots

A set of two calibration plots in the range of 0.1 to 1.0 ppb, and 1.0 to 10.0 ppb of Tl(I) are plotted. They are linear over the entire range.

The minimum detection limit is 0.1 ppb of Tl(I) with a relative mean deviation of $\pm$1.8%.

Interference Study

The procedure is fairly selective and Fe(III), Cr(III), Mn(II), Ni(II), Zn(II), Co(II) and Cu(II) are tolerated in the ratio of 1:240, 1:500, 1:100, 1:1000, 1:300, 1:200 and> 1:1000 respectively at Tl(I) concentration of 5 ppb. Pb(II) interferes seriously with the determination.

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