Potentiometric Determination of Thallium (I) With Hexammine Cobalt (III) Tricarbonato Cobaltate As Redox Titrant

TARIK ABDUL KADHUM NASSER AND MUHAMMAD SALEEM
Faculty of Education, Department of Chemistry, University of Basrah, Basrah, Iraq.

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Introduction

Thallium (I) can be determined by direct or indirect titrimetric or potentiometric oxidizing agents in aqueous and non-aqueous medium. A summary of these methods is given in Table 1 including conditions for titration and range of determinations.

Despite the number of existing titrimetric and potentiometric methods, there is scope for further work on the potentiometric determination of thallium (I). As there are only a limited number of methods reported in the literature (Table 1), most research is now directed to devising a suitable ion selective procedure for the determination of thallium (I), (Table 1).

However due to the simplicity of preparation of hexammine cobalt (III) tricarbonato cobaltate (III) (9) and the low potential of Tl(I) – Tl (III) system compared to the potential of Co (II), Co(III), it was decided to examine the possibility of quantitative measurement of thallium (I) based on its oxidation to thallium (III) by cobalt (III) generated in situ.

The measurement was done potentiometrically. Some of the results of this study are reported in this paper.

Experimental

(1) Hexammine cobalt (III) tricarbonato cobaltate (III). This reagent and its solution was prepared as mentioned in previous publication (9), and it was standardized against ferrous sulphate potentiometrically.
(2) Thallium (I) chloride (100 PPM) solution of Tl(I) was prepared by dissolving (0.2933g) of Tl (I) Cl (BDH) in 250 ml of water and its concentration was checked against potassium dichromate (3). All other reagents used were of analytical grade.

Apparatus

Potential measurements were made with a potentiometer (W.G. Pye & Co. Ltd., Cambridge, England) using platinium as indicating and saturated calomel as reference electrodes.

Procedure

A definite aliquot (0.5 to 20 ml) of thallium (I) chloride solution, previously standardized against potassium dichromate, was taken in a 250 ml glass beaker to which water and HCl were added to get a final volume of 100 ml, (0.1 N with respect to HCl). The titration was done by running in hexammine coblat (III) tricarbonato cobaltate (III) solution from 5.0 ml burette, graduated at 0.02 ml intervals. Slow and constant stirring of the reactants was continued with an electromagnetic stirrer throughout the course of titration.

The potential measurements were recorded when the needle of the potentiometer showed stable reading after each addition. Just before and after equivalence point the addition of the titrant was made in 0.02 ml intervals. The exact volume of the titrant was read from the graph, plotted between mv and volume of the titrant.

Results and Discussion

Different acid strengths were tried to obtain the suitable medium for stoichiometric reaction between Co(III) and Tl(I). Sulphuric acid (1-10N), HCl (1-6N), perchloric acid (1-10%). The reaction was found to proceed quantitatively in 4N HCl. The total reaction could be represented by the following equation:

$$2\,Co^{3+} + Tl^{+} \longrightarrow 2Co^{2+} + Tl^{3+}$$

The oxidation of Tl(I) proceeded to Tl(III) state via Co(III) according to the above equation.

Accordingly, one oxidation step was exhibited on the potentiometric curve.

Table 1
Summary of titrimetric methods for the determination of thallium(I)

Titrant	Medium of titration	Range of determination	Percent relative error	Ref.
$KCLO_3$	5–6M HCl	–	–	1
dichlorobenzene	acetic acid	–	–	2
dichromate	6M HCL	0.05 – 0.63m mole	--	3
dichloramine* T	non-aqueous & Partially aqueous	–	–	4
KIO_3		–	0.2%	5
sodium** tetraphenyl borate	ion-selective electrode	1.3 – 20 mg	0.1 – 10.2	6
water insoluble basic dye salt	ion selective electrode	10 – 1um	–	7
Tungstoarsennate	ion selective	–	–	8

* Potentiometric titration with platinium – SCE system
** Potentiometric titration with liquid – exchanger selective electrode.

The possibility of quantitative relationship is shown in Table 2. Accordingly Tl(I) was determined from 50 ug to 2 mg with maximum relative standard deviation of 0.76%. The effect of foreign ions on the determination of thallium (I) studied by keeping its amount constant and after the addition of interfering ion to it, the titration was carried out and error of determination with varying amounts of various ions was calculated. Results are shown in Table 3.

Table 2
Determination of Tl(I) in 0.1 N HCl

Tl(I) taken mg	Tl(I) found mg	Inflection potential mv	Relative Standard % deviation
0.050	0.051	650	0.50
0.100	0.104	650	0.69
0.200	0.205	750	0.06
0.300	0.295	745	0.23
0.400	0.398	765	0.76
0.500	0.502	750	0.169
1.00	1.010	750	0.15
2.00	2.019	820	0.35

Table 3.
Effect of 1 to 10 mg aluminium (III) on constant amount of thallium(I) (1 mg) in0.1N HCl (inflection potential = 750 mv)

Al^{+++} added mg	Tl^{+} found mg	RSD%
0	1.00	0.300
1	1.015	0.306
2	1.020	0.300
5	1.022	0.250
10	1.020	0.320

Table 4.
Effect of 1 to 10 mg indium (III) on constant amount of thallium(I) (1 mg) in 0.1N HCl (inflection potential = 750 mv)

In^{+++} added mg	Tl^{+} found mg	RSD%
0	1.00	0.300
1	1.010	0.302
2	1.010	0.300
5	1.015	0.200
10	1.01	0.32

Table 5.

Effect of 1 to 10 mg galium (III) on constant amount of thallium (I) (1 mg) in 0.1N HCl (inflection potential = 750 mv).

Ga^{+++} added	Tl^{+} found	RSD %
1	1.010	0.18
2	1.010	0.25
5	1.010	0.30
10		0.32

The method given here for Tl(I) determination is precise, quick and very simple and does not require any special or complex conditions or experience to operate. It seems that chloride ion is catalyzing the conversion of Tl(I) to Tl(III). Such observation can be traced from literature (2-4). Different acids were tried by other workers too to find the most suitable medium. In fact chloride (and to alesser degree bromide) has been found to facilitate the conversion of Tl(I) to Tl(III). This could be the reason why best results are obtained in hydrochloric acid in this work and by other investigators. Moreover, it does not show any appreciable interference of accompanying cations Al(III), In (III) and Ga (III) which are usually present with thallium. Therefore it could be used for the determination of thallium (I) in different samples.

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