C H A P T E R - I I

# ANALYSIS OF THALLIUM(I) BY VANADIUM(V)

The oxidation of thallium (I) and reduction of thallium (III) are facilitated by the presence of chloride[1,2] and sulphate[3] ions respectively. Due to such a change in the behaviour of T (III)/T (I) couple, it was possible to reverse two of the thallium(III) reductions.[1,2] While studying the reaction between vanadium (V) and thallium (I)[2] in hydrochloric acid medium, which is exactly opposite to that of thallium(III)-vanadium (IV)[3] reaction, it was found that 50% of the reaction is completed within 30 minutes at room temperature. Therefore, if the temperature is slightly increased to 40°C, this reaction can be utilized for the analysis of thallium (I) by vanadium (V). The present study gives the results of determination of thallium (I) by this method.

Reagent grade chemicals and doubly distilled water were used throughout this work. Vanadium (V) solutions were prepared by dissolving ammonium vanadate (BDH) in 0.5 mol dm^{-3} in hydrochloric acid and standardized against standard ferrous ammonium sulphate using diphenylamine as indicator. The thallium (I) solutions were obtained by dissolving thallous chloride (BDH) and concentration was determined by titrating with potassium bromate.

Vanadium (IV) solutions were prepared by dissolving vanadyl sulphate (BDH) in water and precipitating the sulphate with barium chloride. The concentration of vanadium (IV) was ascertained by standardizing against standard potassium permanganate. Dissolution of thallic oxide and standardization by iodometry gave the thallium (III) solution. All the absorbance measurements were made on Shimadzu UV-160 A double beam spectrophotometer.

The mechanism of reaction between vanadium (V) and thallium (I) was studied in detail in Chapter-I and it was found that $TlCl_3^{2-}$ and VO_2^+ are the main active species of the reductant and oxidant respectively. The mechanism in terms of these active species is given in Scheme 1. While the added products thallium (III) and

$$TlCl_3^{2-} + VO_2^+ \longrightarrow TlCl_3^- + V(IV)$$

$$TlCl_3^- + VO_2^+ \longrightarrow TlCl_3 + V(IV)$$
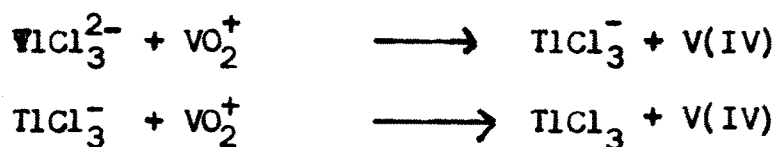
vanadium (IV) did not have any effect on the reaction,

The added chloride also accelerates the reaction which is due to the formation of reactive species of the reductant like $TlCl_3^{2-}$.

The method has been applied to two concentration ranges between 1.0 to 5.0 x 10^{-4} mol dm^{-3} and 2.0 to

5.0×10^{-3} mol dm^{-3}. For the former range of concentration the excess of vanadium (V) was added to the thallium (I) solution containing 4.0 mol dm^{-3} hydrochloric acid and the amount of vanadium (V) reacted was determined by measuring the absorbance at 360 nm at which thallium(III) does not absorb significantly (Figure II(i)). Whereas for the latter range, the amount of vanadium (IV) produced, by the addition of excess vanadium (V) to the thallium(I) solution containing 4.0 mol dm^{-3} hydrochloric acid was determined by measuring the absorbance at 766 nm at which vanadium (IV) has the maximum absorbance (also shown in Figure 1). Beer's law application for both vanadium (V) at 360 nm ($\epsilon = 82.35$) and vanadium (IV) at 766 nm ($\epsilon = 17.77$) under the reaction conditions had been verified earlier between the concentrations 5.6×10^{-4} to 30.08×10^{-4} mol dm^{-3} and 4.97×10^{-4} to 10.0×10^{-3} mol dm^{-3} respectively (Figure I.(i)). (page (18))

Method of analysis :

In the concentration range of $1.0 \times 5.0 \times 10^{-4}$ mol dm^{-3} thallium (I), excess vanadium (V) was added to the solution containing thallium (I) and 4.0 mol dm^{-3} hydrochloric acid. The mixture is then kept in a thermostat to about 30 minutes at 40°C. The mixture is cooled and

Figure 𝕏(𝕚)Spectra of V(V) [———] ,
TI (III) [---------] and V(IV) [—·—·—·] in
solutions containing 4.0 mol dm^{-3} hydrochloric acid*
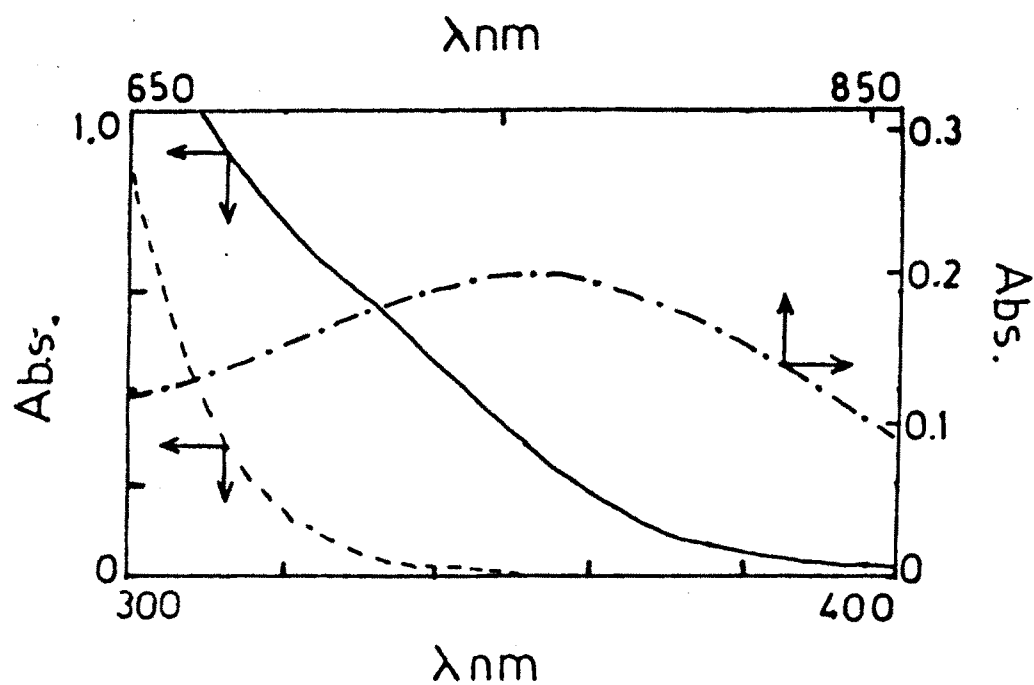
* [V(V)] = 2.0×10^{-3} mol dm^{-3} , [TI(III)] = 1.0×10^{-3} mol dm^{-3}

and [V(IV)] = 1.12×10^{-2} mol dm^{-3}

the absorbance at 360 nm was measured. The absorbance of the solution containing same amount of vanadium (V) and hydrochloric acid was also measured at 360 nm in the absence of thallium (I). From the difference between the two absorbances, ΔA, thallium (I) concentration can be calculated using equation (1),

$$[\text{Tl(I)}] = \frac{\Delta A}{2 \cdot \epsilon} \qquad \qquad \ldots \quad (1)$$

where ϵ is the molare extinction coefficient of vanadium (V) at 360 nm. The factor two in the denominator of equation (1) is due to the stoichiometry of the reaction. The results are shown in Table II(i).

For the latter range of concentrations also excess of vanadium (V) was added to the thallium (I) solution containing 4.0 mol dm^{-3} hydrochloric acid. Because of low solubility, thallous chloride will be precipitated at the beginning which was dissolved completely by shaking and then the mixture was kept in a thermostat at $40^{o}C$ to about 45 minutes. The mixture was cooled and the absorbance at 766 nm was measured. The absorbance at 766 nm of vanadium (V) solution containing 4.0 mol dm^{-3} hydrochloric acid without thallium (I) was also measured. The difference in absorbance, ΔA, was used to calculate thallium (I) concentration from equation 1 by replacing ϵ for the molare extinction coefficient of vanadium (IV) at 766 nm. The results are shown in Table II (ii).

Table II(i) : Results of thallium(I) analysis obtained
from absorbance measurements at 360 nm

$[HCl] = 4.0$ mol dm^{-3}

$[Tl(I)]x10^4$ mol dm^{-3}		Error	$[Tl(I)]x10^4$ mol dm^{-3}		Error
Taken	Found	%	Taken	Found	%
1.00	1.00	-	3.50	3.49	0.3
1.50	1.49	0.6	3.75	3.79	1.0
1.75	1.73	1.1	4.00	3.98	0.5
2.25	2.22	1.3	4.25	4.22	0.7
2.50	2.46	1.6	4.50	4.46	0.9
3.00	3.01	0.3	4.75	4.70	1.0
3.25	3.31	1.8	5.00	4.95	1.0

Table II(ii) : Results of thallium(I) analysis obtained
from the absorbance measurements at
766 nm.

$[HCl] = 4.0$ mol dm^{-3}

$[Tl(I)] \times 10^{-3}$ mol dm^{-3}		Error %
Taken	Found	
2.0	1.99	0.5
2.5	2.48	0.8
3.0	3.06	2.0
3.5	3.49	0.3
4.0	3.97	0.75
5.0	4.92	1.6

Since, this is a redox method of analysis the ions reacting with either the reactants, V(V) and Tl(I), or the products V(IV) and Tl(III) may interfere in this method. Further due to behaviour of Tl(III)/Tl(I) couple, as mentioned earlier, sulphate will interfere in this method.

References :

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