Complexometric titration of thallium(III) using 3-mercapto-1, 2-propanediol as demasking agent

Prakash Shetty* A M A Khader®, A Nityananda Shetty® & R V Gadagc

*Department of Chemistry, Nitte Mahalinga Adyanthaya Memorial Institute of Technology, Nitte 574 110, India
®Department of Post Graduate Studies and Research, Mangalore University, Mangalagangothri 574 199, India
cDepartment of Chemistry, Karrataka Regional Engineering College, Surathkal, Srinivasnagar 574 157, India

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A simple and selective EDTA method involving masking and demasking technique is proposed for the determination of thallium(III) using 3-mercapto-1, 2-propanediol as releasing agent. Reproducible and accurate results are obtained in the range 4-75 mg of thallium with relative error of ±0.3% and coefficient of variation not more than 0.46%.

The literature survey reveals that thiopyrene1, thiosemicarbazide2, hydrazine sulphate3 and 4-amino-5-mercapto-3-propyl-1, 2, 4-triazole4 are some of the reagents which have been proposed as selective masking agents in the complexometric determination of thallium(III) by releasing EDTA from TI-EDTA complex. In the present study, complexometric determination of thallium(III) using 3-mercapto-1, 2-propanediol has been attempted with success and the results are reported herein.

Experimental procedure—All chemicals used were of AR grade. An aqueous 1% solution of 3-mercapto-1, 2-propanediol was prepared. Thallic nitrate solution was prepared by reported procedures and standardised by chromate method6. Zinc sulphate solution (~0.02 M) was standardised by quinaldinate method6. EDTA solution (~0.04 M) was prepared by dissolving the disodium salt of EDTA in deionised water. An aqueous solution of xylenol orange (0.5%) was used as an indicator.

To an aliquot of the solution containing 4-75 mg of Ti(III), and associated ions, an excess 0.04 M EDTA solution was added. The solution was diluted to about 50 mL with distilled water and the pH is adjusted to 5-6 with solid hexamine or with acetic acid-sodium acetate buffer. The surplus EDTA was titrated with 0.02 M zinc sulphate solution to the sharp colour change of xylenol orange to red-violet. A 1% solution of 3-mercapto-1, 2-propanediol in water (just above 1:3 molar ratio of metal to ligand) was added, the mixture shaken well and allowed to stand for 5 min to complete the EDTA release. The released EDTA was titrated with zinc sulphate solution as before. The second titre value corresponds to the thallium content in the aliquot.

Thallium(III) complexes with some sulphur donor ligands were prepared by the reported methods7 and their purity was checked by the elemental analysis. About 0.3 g of the complex was decomposed with aqua-regia and the solution was evaporated to near dryness. The residue was then cooled, dissolved in 2 N HNO3 (about 3 mL) and the volume was made up to 250 mL with deionised water. Aliquots of the made up solution were used for titration as per above procedure.

Results and Discussion

Effect of excess reagent—Preliminary investigations showed that addition of 3-mercapto-1, 2-propanediol in 1:3 molar ratio (M:L) was sufficient for the quantitative and instantaneous release of EDTA from TI-EDTA complex at room temperature. However, no adverse effects were observed even on adding excess reagent. In all subsequent determinations, the concentration of the reagent was maintained slightly above the molar ratio 1:3 (M:L).

Accuracy and precision—To find out the accuracy and precision of the method, several determinations of thallium at different concentration level were carried out under experimental conditions. The results obtained were reproducible and accurate in the range 4-75 mg with relative error and coefficient of variation not exceeding ±0.3% and ±0.46%, respectively.

Effect of foreign ions—The effect of diverse metal ions on the accuracy and precision of the method for the determination of Ti(III), was examined by estimating 19.80 mg of Ti(III) in presence of diverse ions. Metal ions Ti(III) (200 mg), Pb(II) (200), Cu(II) (70), Ni(II) (100), Cd(II) (100), Co(II) (120), Fe(III) (80), Al(III) (80), Ti(IV) (70), Mo(VI) (70) and Mn(II) (30), do not show interference. Anions like sulphate (150), chloride (100), nitrate (150), tartrate (200) and oxalate (200) also do not show any interference. Cations like Pd(II), Hg(II), Sn(IV), Bi(III) and Cr(III) cause severe interference. But the interference of Pd(II) and Sn(IV) can be avoided by using L-histidine and sodium fluoride, respectively, as secondary masking agents.
with EDTA in its monovalent state. Even if thallium (I) forms a complex with EDTA, it may do so only in basic medium (pH 8-9), but complete decomposition of Tl(I)-EDTA complex takes place in the acidic medium. Therefore, the redox system Tl(I)-Tl(III) can be conveniently employed in acidic medium for its complexometric determination. 3-Mercapto-1,2-propanediol selectively releases EDTA from Tl(III)-EDTA complex through the reduction of Tl(II) to Tl(I) for which a one electron change per thiol group occurs. The Tl(I) so formed is complexed with the reagent.

The release of EDTA from Tl(III)-EDTA complex is instantaneous at room temperature itself. Therefore, the method does not require heating after the addition of the reagent. The reagent forms a soluble complex with Tl(I).

Applications—The present method has been successfully used for the determination of thallium in its complexes with mercapto-ligands and in artificial mixtures of thallium(III) salt. The results are summarised in Tables 1 and 2, which suggest that the method can be conveniently used in the accurate analysis of thallium complexes, mixtures of ions and Tl(III) in presence of Tl(I).

Mechanism of demasking—Thallium forms a stable complex with EDTA in its trivalent state (log $K = 22.5$), but shows little tendency for complexation

### Table 1—Analysis of thallium complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Thallium calculated, %</th>
<th>Thallium found, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl(C$_2$H$_5$N$_4$S)$_2$</td>
<td>61.30</td>
<td>61.24</td>
</tr>
<tr>
<td>Tl(C$_2$H$_5$N$_4$S)$_2$</td>
<td>60.73</td>
<td>60.86</td>
</tr>
</tbody>
</table>

$^1$Thallium complex of 4-amino-5-mercapto-3-methyl-1,2,4-triazole.

$^2$Thallium complex of 5-amino-2-mercapto-1,3,4-thiadiazole.

### Table 2—Determination of thallium in artificial mixtures

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Quantity added, %</th>
<th>Thallium* present, %</th>
<th>Thallium** found, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II) + Cu(II)</td>
<td>40.2 + 20.1</td>
<td>39.70</td>
<td>39.62</td>
</tr>
<tr>
<td>Pb(II) + Ni(II)</td>
<td>43.0 + 28.6</td>
<td>28.40</td>
<td>28.44</td>
</tr>
<tr>
<td>Pb(II) + Cd(II)</td>
<td>50.1 + 40.0</td>
<td>9.90</td>
<td>9.88</td>
</tr>
<tr>
<td>Pb(II) + Co(II)</td>
<td>44.6 + 33.4</td>
<td>22.00</td>
<td>22.04</td>
</tr>
</tbody>
</table>

*By difference

**Average of three determinations.

References