Rapid Spectrophotometric Determination of Thallium with Mepazine Hydrochloride

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Mepazine hydrochloride reacts with thallium(III) at room temperature in phosphoric acid medium to give an orange-red species with an absorption maximum at 512 nm. The reaction obeys Beer's law over the concentration range 0.1-13.0 µg/ml of thallium(III) with an effective spectrophotometric range of 1.8-11.0 µg/ml. The molar absorptivity is $1.60 \times 10^{4}$ dm$^3$ mol$^{-1}$ cm$^{-1}$. The efficacy of the method is shown by the successful determination of thallium in synthetic thallium alloys.

Determination of microgram amounts of thallium is of great importance because of its toxic nature and its increasing industrial applications. Most of the reagents proposed for the spectrophotometric determination of thallium are extraction-photometric reagents. During the course of our investigations on the analytical applications of N-alkyl derivatives of phenothiazines, it was found that 10-[(1-methyl-3-piperidyl)methyl] phenothiazine hydrochloride or mepazine hydrochloride [MH] forms an orange-red species with thallium(III) in acid solution at room temperature. This colour reaction has been used for the rapid spectrophotometric determination of thallium(III). The proposed method offers the advantages of simplicity, rapidity, reasonable selectivity and sensitivity and wider range of determination without the need for extraction or heating.

A stock solution of thallium(III) was prepared by adding bromine water to requisite quantity of thallium(I) sulphate dissolved in doubly distilled water until a faint yellow colour persisted and heating the solution carefully to remove the excess of bromine. The solution was cooled, diluted to 100 ml and standardised volumetrically. The stock solution was further diluted to give a standard solution containing 100 µg/ml of thallium(III). The reagent solution (0.2% wt/v) was prepared in doubly distilled water and stored in an amber glass bottle in a refrigerator. Solutions of foreign ions of suitable concentrations were prepared using AR grade reagents. A Hitachi 150-20 spectrophotometer with matched 1 cm quartz cells was used for absorbance measurements.

Procedure

To an aliquot of the sample solution containing 45-275 µg of thallium(III), 10 $M$ phosphoric acid (8 ml) and 0.2% MH solution (8 ml) were added. The mixture was diluted to 25 ml with doubly distilled water and the absorbance was measured at 512 nm against a reagent blank. The thallium(III) content was determined from the standard calibration graph.

Mepazine hydrochloride reacts with thallium(III) instantaneously at room temperature (26±2°C) in sulphuric or phosphoric acid medium to form an orange-red species believed to be a radical cation. The sensitivity of the reaction and the stability of the orange-red species are almost the same in both sulphuric and phosphoric acid media. Thallium(III) can be determined spectrophotometrically in sulphuric acid medium, but many common ions such as Fe(III), Cu(II), Se(IV), Hg(II) and Pb(II) interfere in the determination. Hence, phosphoric acid (3$M$) is recommended as the maximum absorbance is observed instantaneously in 2-5$M$ phosphoric acid medium. The absorbance decreases below this acidity range and slightly increases above this range.

The orange-red species exhibits maximum absorbance at 512 nm. The absorbance of thallium(III) solution and the reagent blank is negligible at this wave length. A 31-fold molar excess of the reagent was found necessary for maximum colour intensity. The absorbance remained constant for at least 1 h. The temperature had no effect on the absorbance over the range 5-45°C. The absorbance remained unchanged within the limit of experimental error when the order of addition of reactants was varied.

The system obeys Beer's law in the range 0.1-13.0 µg/ml of Tl(III). The optimum concentration range for the effective spectrophotometric determination of thallium as evaluated by Ringbom's method is 1.8-11.0 µg/ml of Tl(III). According to Sandell's expression, the sensitivity of the reaction is 12.2 ng cm$^{-2}$ and the molar absorptivity is $1.60 \times 10^{4}$ dm$^3$ mol$^{-1}$ cm$^{-1}$. The standard deviation calculated from five determinations in a solution containing 4 µg/ml of Th(III) is 0.03 and the relative error is less than ±2%.

The extent of interference by foreign ions associated with thallium in its alloys and minerals was determined by measuring the absorbance of a so-
Table 1 – Determination of Thallium in Its Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Tl taken (ppm)</th>
<th>Tl found (ppm)</th>
<th>Rel. error (%)</th>
<th>St. deviation (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antrification alloy</td>
<td>2% Tl, 98% Cu</td>
<td>2.00</td>
<td>2.02</td>
<td>+1.00</td>
<td>0.03</td>
</tr>
<tr>
<td>Low melting alloy</td>
<td>8.9% Tl, 44.2% Bi, 35.8% Pb, 11.1% Cd</td>
<td>6.00</td>
<td>6.05</td>
<td>+0.83</td>
<td>0.02</td>
</tr>
<tr>
<td>Low melting alloy</td>
<td>7% Tl, 52% Bi, 34% Pb, 7% Cd</td>
<td>3.50</td>
<td>3.48</td>
<td>-0.57</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Average of five determinations.

The method was applied to the determination of thallium in Tl–Cu alloy (antrification alloy) and Tl–Bi–Pb–Cd alloys (low melting alloys). As analysed samples of these alloys were not available, synthetic mixtures corresponding to the compositions of these alloys were prepared and thallium content was determined following the standard procedure described earlier. The results are presented in Table 1. The results show that thallium can be determined in presence of other metal ions.

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References