Solvent extraction and determination of mercury(II) using triphenylarsine oxide

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A method has been described for quantitative extraction of mercury(II) from 0.5-0.6 mol dm$^{-3}$ sodium salicylate media using 0.5% triphenylarsine oxide dissolved in toluene as an extractant. Mercury(II) is determined spectrophotometrically after complexation with 1-2(pyridylazo)-2-naphthol in the organic phase. The probable extracted species is Hg(HSal)$_2$.2TPASO. The method is applicable to the analysis of mercury(II) in industrial effluents, ayurvedic medicines and commercial products.

Various extractants such as mesityl oxide$^1$, diocetylarsinic acid$^2$, caproic acid$^3$ and trioctylamine$^4$ have been used for the extraction of mercury(II). Besides, triphenylphosphine oxide$^5$ and tris-2-(ethylhexyl) phosphate$^6$ have also been explored as potential extractants for mercury(II).

However, no work is reported for the extraction of mercury from salicylate media using arsenic bonded oxygen donor extractant. In this note we propose triphenylarsine oxide (TPASO) as an extractant for mercury(II).

Experimental

Stock solution of mercury(II) was prepared by dissolving 0.338 g of mercuric chloride in 250 ml distilled water containing minimum amount of hydrochloric acid. The solution was standardised by literature method$^7$. Working solutions of required concentration were prepared by suitable dilution. A 0.5% solution of triphenylarsine oxide (TPASO) (Fluka) dissolved in toluene was used for the extraction studies. A buffer solution of pH 10 was prepared from 0.01 mol dm$^{-3}$ sodium carbonate and 0.01 mol dm$^{-3}$ sodium hydrogen carbonate solutions. A 0.1% methanolic solution of 1-2 (pyridylazo) 2-naphthol (PAN) was used for the spectrophotometric estimation of mercury(II) in TPASO phase. All chemicals used were of AR grade.

Results and discussion

The optimum conditions for the quantitative extraction of mercury(II) were established by varying pH (4-10), sodium salicylate concentration (5 x 10$^{-2}$ - 6.5 x 10$^{-1}$ mol dm$^{-3}$) and TPASO concentration (0.05 - 0.5%) using toluene as the diluent. The quantitative extraction of mercury (II) (5-50 μg) was feasible from 0.5-0.6 mol dm$^{-3}$ sodium salicylate solution at pH 5.5-6.0 using 5 ml of 0.5% TPASO dissolved in toluene [or 2 x 5 ml of 0.5% TPASO dissolved in toluene for milligram amounts of mercury(II) (1-5 mg)]. A shaking period of 60 s was adequate for the quantitative extraction of mercury(II).
Of the several diluents tried, toluene, xylene and benzene gave quantitative extraction of mercury(II) whereas with chloroform and carbon tetrachloride the extraction was incomplete (61.8-87.1%). Toluene, as it gave faster and clear separation, was used for further extraction studies.

Various stripping agents of different concentrations were examined for the back-extraction of mercury(II) from the organic phase. The quantitative stripping of mercury(II) was possible with two 5 ml portions of hydrochloric acid (0.5-1 mol dm\(^{-3}\)) and ammonium hydroxide (0.5-2 mol dm\(^{-3}\)). Water does not strip mercury(II) from the TPASO phase.

A plot of log of distribution ratio versus log of salicylate concentration gave a slope of 2.0 indicating metal to salicylate ratio of 1:2, indicating the formation of Hg(HSal). While a plot of log of distribution ratio versus log of TPASO concentration at fixed pH (5.5) and salicylate concentration (0.5 mol dm\(^{-3}\)) gave a slope of 2.0 indicating the presence of two TPASO molecules.

The red coloured Hg-PAN complex was stable for 24 h and showed \(\lambda_{\text{max}}\) at 570 nm. Beer’s law was obeyed in the range of 0.1 - 10 \(\mu\)g ml\(^{-1}\) with coefficient of variation 0.9%. Sandell’s sensitivity and molar absorptivity was 0.02 \(\mu\)g cm\(^{-2}\) and 0.8864 \(\times\) 10\(^4\) mol\(^{-1}\) cm\(^{-1}\), respectively.

### Analysis of Hg(II) in real samples

The suitability of the proposed method was tested by applying it to the estimation of mercury(II) in various medicinal samples, waste water samples and commercial product.

Untreated effluents (samples A and B) from industrial manufacturers of caustic soda, liquid chlorine, rayon textile and sulphuric acid were evaporated to reduce the volume to about 15 ml and digested with 5 ml of conc. nitric acid for 10 min, filtered and finally diluted to 25 ml with distilled water. An aliquot of this solution was then taken for analysis by the recommended procedure. The results obtained by the proposed method were found to be in good agreement with those obtained by the Central Laboratory, Maharashtra Pollution Control Board (New Bombay, India), using AAS.

The method was also applied for the analysis of mercury in ayurvedic medicine; Rasa Sindooram (Kottakal Arya Vaidya Sala, Kerala, India) and mercurochrome solution. About 10 mg of ayurvedic sample was dissolved in 5 ml of aqua regia, evaporated to incipient dryness, extracted with distilled water and filtered. The filtrate was then diluted to 100 ml. An aliquot of this solution was taken for the estimation of mercury(II) by the proposed method.

Mercurochrome solution (5 ml) was treated with 4 ml of 10 mol dm\(^{-3}\) sulphuric acid and filtered. The filtrate was then diluted to 250 ml with distilled water and filtered. The results obtained are presented in Table I.

### Table I -- Estimation of mercury (II) in industrial effluents, ayurvedic medicines and other commercial products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>AAS</th>
<th>Proposed Method*</th>
<th>C.V. (%)</th>
</tr>
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<tbody>
<tr>
<td><strong>Industrial effluents</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample A (from rayon textile and caustic</td>
<td>4.975 mg ml(^{-1})</td>
<td>4.92 mg ml(^{-1})</td>
<td>0.92</td>
</tr>
<tr>
<td>soda industry)</td>
<td></td>
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<tr>
<td>Sample B (from liquid chlorine, caustic</td>
<td>31.01 mg ml(^{-1})</td>
<td>30.7 mg ml(^{-1})</td>
<td>0.11</td>
</tr>
<tr>
<td>soda sulphuric acid and industries)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merbromine solution (Mercurochrome 2% m/v)</td>
<td>0.53%</td>
<td>0.51%</td>
<td>0.4</td>
</tr>
<tr>
<td>Ayurvedic medicine Rasa Sindooram (Kottakal</td>
<td>219 (\mu)g ml(^{-1})</td>
<td>217.2 (\mu)g ml(^{-1})</td>
<td>0.25</td>
</tr>
<tr>
<td>Arya Vaidya Sala, Kerala, India)</td>
<td></td>
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<tr>
<td>“Neko” medicated soap (Parke Davis [J] Ltd.)</td>
<td>0.44%</td>
<td>0.43%</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*Average of triplicate analysis
water. An aliquot was taken for the extraction and spectrophotometric determination of mercury(II) by the general procedure.

A 200 mg sample of medicated soap was dissolved in distilled water containing 5 ml of concentrated hydrochloric acid. The solution was heated for 5 min, cooled and diluted to 100 ml with distilled water. An aliquot was then analysed for its mercury(II) content by the proposed method.

The results of the recovery of mercury(II) by the proposed method are in good agreement with those obtained by the AAS method and are reported in Table 1.

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References