2.1 INTRODUCTION

Mercury has been extensively used in the production of electrical goods, pulp and paper products, paints, dental applications and pesticide formulations. About half of the anthropogenic input to the environment has come from manufacturing caustic soda and chlorine by the electrolysis of brine. Because of such a wide use and the volatility of some species, mercury is now a global pollutant which has been measured in the deep ocean, the atmosphere, Antarctica and Arctic.

Mercury is found at trace levels in many minerals, with continental rocks containing an average of 80 µg/kg [1]. Soil mercury concentrations may vary dramatically depending on the local geology and industry. Typically soils are reported to contain 0.01-0.5µg/g [2]. Mercury is normally present in plant tissues in the range 30-700µg/g [3]. Mercury concentrations in water at various typical levels are reported as ranging from 0.0001 to 2.8 µg/l in freshwater, and from 0.01 to 0.22 µg/l in sea water [4].

The mercury poisoning in human is measured by the analysis of blood, tissues, urine, serum and hair samples. Mathews [5] has reported elevated levels of mercury in blood and hair as a result of consuming fish contaminated with mercury. In the 1950’s and 1960’s two major epidemics of methyl mercury poisoning through the fish consumption occurred in Minnamata Bay and Niigata (both in Japan) where thousands of people were affected [6]. Hair is a suitable indicator for monitoring of human exposure to mercury, which reflects organic mercury in hair when exposure is prolonged and relatively constant. The straight
line fitted to the data obtained on mercury(II) analysis of hair and blood samples are related by,

\[
\text{Hair mercury} = 0.367 \times \text{blood mercury} + 0.694
\]

where the mercury concentration is expressed in µg. However, it is easier to monitor the levels of mercury in hair rather than blood samples. In hair, mercury exists in the form of methyl mercury. Methyl mercury in hair is analysed through a three step procedure – digestion, extraction and determination. Digestion is an essential step for the release of methyl mercury bound to hair with cystine sulphur or the sulphhydryl (SH) group in amino acids [7]. The digestion step can break the existing bonds between hair and methyl mercury. Two kinds of heated digestions have been used, either acidic [8] or basic [9]. In view of the low levels of mercury, it is often followed by extraction with suitable solvents [10] or solid phase supports. However, the latter approach is preferred due to the advantages like low solvent consumption, absence of emulsion etc.

Various solid supports have been used for mercury (II) extraction. Among these silica gel [11-14], ion-exchange resins [15], natural clays [16] and naphthalene [17-19] are promising supports. The latter sorbent is preferred in view of the easy dissolution in acetone or dimethyl formamide for subsequent determination by spectrophotometry. This eliminates the tedious elution step.

Molten naphthalene was used as an extractant in the initial stages for the preconcentration of inorganics [20]. However, this technique is not suitable for preconcentrating metals which form thermally unstable complexes [21]. Subsequently, the solid-liquid separation after coprecipitative preconcentration of metal chelates onto microcrystalline naphthalene was widely used as it is rapid, economical and can be applied to many types of complexes. This technique is especially attractive for complexes that have poor solubility in organic solvents [22]. The only difficulty is in the filtrations of small amounts of naphthalene. Hence, column preconcentration using naphthalene is being recently employed for the preconcentration of trace and ultra trace amounts of inorganics [23]. These procedures are really time consuming as 6-8 h is required for preconcentration of
inorganics present in 1.0 l of sample solution. In view of this, batch preconcentration procedures still play significant role in preconcentration of inorganics from dilute aqueous solutions. Table 2.1 summarizes the salient features of preconcentration procedures developed for mercury(II) using naphthalene as collector.

Table 2.1 Summary of preconcentration procedures developed for mercury (II) using naphthalene as collector

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Detection method</th>
<th>Reagent</th>
<th>pH</th>
<th>Detection limit (µg/ml)</th>
<th>Linear range (µg/ml)</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anodic stripping - differential pulse voltammetry</td>
<td>Methyl trioctyl ammonium chloride</td>
<td>-</td>
<td>0.13</td>
<td>1.2-8.7</td>
<td>Natural waters, waste water, synthetic samples</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>CVAAS</td>
<td>Dithizone</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Water samples</td>
<td>19</td>
</tr>
</tbody>
</table>

In all the above described procedures, metal complexes are coprecipitated onto microcrystalline naphthalene. In the present work, metal chelates were not adsorbed, instead chelate modified naphthalene was used for adsorbing metal ions. Taking into account the high affinity of mercury species to organic reagents with sulfur donor atoms, quinoline-8-thiol was selected for possible SPE preconcentration of mercury (II).

Thus, in the method described below, mercury(II) is selectively preconcentrated by using quinoline-8-thiol modified naphthalene as solid phase extractant (SPE). The SPE can be prepared simply by pouring an acetone solution of naphthalene and the reagent into water. The material prepared is used for the preconcentration of mercury (II). Further, mercury (II) preconcentrated on naphthalene is filtered and dissolved in acetone for determined subsequently by spectrophotometry using dithizone procedure [25]. Various parameters that
influence the preconcentration of mercury (II) by solid phase extraction were systematically optimized and the results obtained are discussed in the following pages.

2.2 PRELIMINARY INVESTIGATIONS

The solid phase extraction of 10 µg of mercury (II) present in 250 ml of aqueous solution was carried out by adjusting the pH to 6.0 in the presence of 10 ml of 1.0 M sodium acetate-acetic acid buffer onto 0.5 g of quinoline-8-thiol modified naphthalene. The mercury (II) preconcentrated onto quinoline-8-thiol modified naphthalene was dissolved in 2 ml of acetone. To the above acetone solution, 2.5 ml each of 5.0 M sulphuric acid and 6.0 M acetic acid were added, diluted to 15 ml with chloroform equilibrated water and shaken for 1 min with 5 ml of dithizone in chloroform. The chloroform layer was collected over anhydrous sodium sulphate and the absorbance of mercury - dithizone complex was measured at 500 nm. The mechanism of SPE of mercury(II) using quinoline-8-thiol modified naphthalene is given in Fig.2.1.

2.3 OPTIMIZATION OF MAIN EXPERIMENTAL VARIABLES

2.3.1 Effect of pH

The effect of pH on the preconcentration of 10 µg of mercury (II) present in 250 ml of aqueous phase onto 0.5 g of quinoline-8-thiol modified naphthalene was studied in the pH range 2.0-10.0 in steps of 1.0. The mercury (II) preconcentrated onto quinoline-8-thiol modified naphthalene was determined after the dissolution of SPE in acetone and determined by using dithizone procedure. The extraction of mercury(II) onto quinoline-8-thiol modified naphthalene is constant (Fig.2.2) and maximum in the pH range 5.0-7.0. In all subsequent experiments, the pH was adjusted to 6.0±1.0 using ammonium acetate buffer.
Fig. 2.1 Mechanism of SPE of mercury (II) using quinoline-8-thiol modified naphthalene.
2.3.2 Effect of Quinoline-8-thiol concentration in naphthalene

The quinoline-8-thiol concentration in naphthalene was varied from 0.1-10%. Mercury (II) enriched onto quinoline-8-thiol modified naphthalene was determined spectrophotometrically using dithizone as reagent. The results obtained are shown in Figure 2.3. The enrichment of mercury(II) onto quinoline-8-thiol modified naphthalene was quantitative when the concentration of quinoline-8-thiol is more than 1%. Hence, in all subsequent experiments, 1% quinoline-8-thiol modified naphthalene was used. Further, a minimum of 0.5g of 1% quinoline-8-thiol modified naphthalene is essential for quantitative enrichment of mercury(II).
2.3.3 Effect of time of stirring

The time of stirring was varied from 5 to 60 minutes during the preconcentration of mercury (II) onto quinoline-8-thiol modified naphthalene. The determination of mercury (II) enriched on to quinoline 8-thiol modified naphthalene was carried out as described in section 2.3.1. The results obtained are shown in figure 2.4. It is clear that a minimum of 15 minute of stirring time was enough for quantitative enrichment of mercury (II). In all subsequent experiments 15 minute stirring time was used.

2.3.4 Effect of aqueous phase volume

The effect of aqueous phase volume on the preconcentration of mercury (II) onto quinoline-8-thiol modified naphthalene in the range 10-250 ml was studied. The preconcentrated mercury (II) onto quinoline-8-thiol modified naphthalene was determined by dithizone procedure as described in Section 2.3.1. The results obtained (Table 2.2) indicate that quantitative preconcentration of mercury (II) was observed up to 250 ml and thus enabling enrichment factor of 50.
2.4. CALIBRATION GRAPH, SENSITIVITY AND PRECISION

A series of solutions containing 0.5 to 50 μg of mercury (II) was diluted to 25 ml and pH was adjusted to 6.0 ± 1.0 by using ammonium acetate buffer. 5 g of quinoline-8-thiol modified naphthalene was dispersed in the above solution and stirred for 1 min. The solution was filtered and the residue obtained was dissolved in acetone and transferred to 25 ml each of 10% sulphuric acid and acetic acid solutions of dimethylformamide. The mixture was shaken for about 1 min. The organic layers were separated and collected in the 10 ml calibration standard flask and the absorbance was determined at the optimum conditions described above. The calibration curve was plotted for the concentration range 0.5-50 μg present in 25 ml of the solution. The standard deviations were determined three times over the concentration range and were 1.05 ± 15%.

2.4.5 Choice of solvent

Various solvents were tested for the dissolution of the mercury chelate of quinoline-8-thiol together with naphthalene. This material was found to be insoluble in many non-aqueous solvents but dissolved easily in water miscible solvents like acetone, DMF, acetonitrile and DMSO. 2 ml of acetone or DMF were enough for the dissolution of 0.5 g of mercury (II) adsorbed quinoline-8-thiol modified naphthalene. On the other hand, 2.5 and 5.0 ml of acetonitrile and DMSO were required for complete dissolution. Hence, acetone was chosen in further studies in view of high solubility and low cost.
2.4 CALIBRATION GRAPH, SENSITIVITY AND PRECISION

A series of solutions containing 0.5 to 50 µg of mercury (II) was diluted to 250ml and the pH was adjusted to 6.0 ± 1.0 by using ammonium acetate buffer. 0.5g of quinoline-8-thiol modified naphthalene was added to the above solution and stirred for 15 minutes. The solution was filtered and the residue obtained was dissolved in 2 ml of acetone and transferred in to separating funnel containing 10ml of chloroform equilibrated water, 2.5ml each of 5.0M sulphuric acid and acetic acid and 5ml dithizone in CHCl₃. The mixture was shaken for about 1 min. The organic layer was separated and collected in the 10 ml dry standard flask and the absorbance was measured at 500nm [25]. Under the optimum conditions described above, the calibration curve (Fig.2.5) was linear over the concentration range 0.5-50 µg present in 250 ml of the sample solution.

Ten replicate determinations of 10 µg of mercury (II) present in 250 ml of the solution gave a mean absorbance of 0.206 with a relative standard deviation of 1.95% (cf. Table 2.3). The limit of detection (lowest concentration below which recoveries becomes non quantitative) corresponding to three times the standard deviation of the blank (3σ) was found to be 2µg/l. All the statistical calculations are based on the average of triplicate readings for each standard solutions in the given range.

2.5 EFFECT OF DIVERSE IONS

Sample solutions containing 10 µg of mercury(II) and various amounts of different metal ions were subjected to preconcentration and determination by following the procedure described in Section 2.4. The tolerance limit (error < 3%) are given in Table 2.4. From the table, no interference was observed due to 100-fold amounts of Li(I), Na(I), K(I), Ca(II), Ba(II), Sr(II), Be(II), Pb(II), Co(II), Ni(II), Al(III), La(III), Zr(IV), Th(IV), U(VI), NO₂⁻, Cl⁻, NO₃⁻, SO₄²⁻, 50 fold amounts of Cd(II), Cu(II) and Cr(III) and 10 fold amounts of Mn(II), Fe(II),
Te(IV), V(V) and Mo(VI). Further, equal amounts of Sb(III) and Cr(VI) also did not interfere in the above developed preconcentration procedure.

![Calibration graph](image)

**Fig. 2.5 Calibration graph**

**Table 2.3 Precision studies**

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Absorbance</th>
<th>Hg(II) found (µg)</th>
<th>$\bar{X}_i - \bar{X}$</th>
<th>$(X_i - \bar{X})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.202</td>
<td>9.80</td>
<td>-0.20</td>
<td>0.0400</td>
</tr>
<tr>
<td>2</td>
<td>0.208</td>
<td>10.09</td>
<td>0.09</td>
<td>0.0081</td>
</tr>
<tr>
<td>3</td>
<td>0.205</td>
<td>9.95</td>
<td>-0.05</td>
<td>0.0025</td>
</tr>
<tr>
<td>4</td>
<td>0.206</td>
<td>10.00</td>
<td>0.00</td>
<td>0.0000</td>
</tr>
<tr>
<td>5</td>
<td>0.210</td>
<td>10.19</td>
<td>0.19</td>
<td>0.0361</td>
</tr>
<tr>
<td>6</td>
<td>0.199</td>
<td>9.66</td>
<td>-0.34</td>
<td>0.1156</td>
</tr>
<tr>
<td>7</td>
<td>0.210</td>
<td>10.24</td>
<td>0.24</td>
<td>0.0576</td>
</tr>
<tr>
<td>8</td>
<td>0.202</td>
<td>9.81</td>
<td>-0.19</td>
<td>0.0361</td>
</tr>
<tr>
<td>9</td>
<td>0.208</td>
<td>10.10</td>
<td>0.10</td>
<td>0.0100</td>
</tr>
<tr>
<td>10</td>
<td>0.210</td>
<td>10.19</td>
<td>0.19</td>
<td>0.0361</td>
</tr>
</tbody>
</table>

$\bar{X}_i = 10.00 \quad \Sigma (X_i - \bar{X})^2 = 0.3441$

$$\sigma = \sqrt{\frac{\Sigma (X_i - \bar{X})^2}{n - 1}}$$

$$\sigma = \sqrt{\frac{0.3441}{9}} = 0.1949$$
Table 2.4 Effect of diverse ions

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Ion</th>
<th>Compound taken</th>
<th>Tolerance limit*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li</td>
<td>Li₂CO₃</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Na</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>K</td>
<td>KCl</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Ca</td>
<td>Ca(OH)₂</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Ba</td>
<td>BaCl₂.2H₂O</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>Sr</td>
<td>SrCl₂.6H₂O</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>Be</td>
<td>BeSO₄.4H₂O</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>Cd</td>
<td>3CdSO₄.8H₂O</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>Pb</td>
<td>Pb(NO₃)₂</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>Zn</td>
<td>ZnO</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>Co(II)</td>
<td>Co(NO₃)₂.6H₂O</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>Mn(II)</td>
<td>MnCl₂.4H₂O</td>
<td>10</td>
</tr>
<tr>
<td>13</td>
<td>Cu(II)</td>
<td>CuSO₄.5H₂O</td>
<td>50</td>
</tr>
<tr>
<td>14</td>
<td>Fe(III)</td>
<td>FeCl₃</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>Al(III)</td>
<td>Al₂O₃</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>Sb(III)</td>
<td>Sb₂O₃</td>
<td>1</td>
</tr>
<tr>
<td>17</td>
<td>La(III)</td>
<td>La(NO₃)₃.6H₂O</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>Bi(III)</td>
<td>Bi(NO₃)₃.5H₂O</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>Zr(IV)</td>
<td>ZrOCl₂.8H₂O</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>Th(IV)</td>
<td>Th(NO₃)₄.6H₂O</td>
<td>10</td>
</tr>
<tr>
<td>21</td>
<td>U(VI)</td>
<td>UO₅(CH₃COO)₂.2H₂O</td>
<td>100</td>
</tr>
<tr>
<td>22</td>
<td>Te(IV)</td>
<td>TeCl₄</td>
<td>10</td>
</tr>
<tr>
<td>23</td>
<td>Mo(VI)</td>
<td>Na₂MoO₄.2H₂O</td>
<td>10</td>
</tr>
<tr>
<td>24</td>
<td>Cr(VI)</td>
<td>K₂Cr₂O₇</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>Br⁻</td>
<td>KBr</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>I⁻</td>
<td>KI</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>NO₂⁻</td>
<td>NaN₂O₂</td>
<td>100</td>
</tr>
<tr>
<td>28</td>
<td>SCN⁻</td>
<td>KSCN</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>AsO₄³⁻</td>
<td>Na₂HAsO₄.7H₂O</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>VO₄³⁻</td>
<td>Na₃VO₄.H₂O</td>
<td>-</td>
</tr>
</tbody>
</table>

*Maximum Interferent tested = 1000 µg
## 2.6 SPECTRAL STUDIES

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Spectral Data</th>
</tr>
</thead>
</table>
| A: Naphthalene                  | IR: 3040 cm\(^{-1}\), 1610 cm\(^{-1}\)  
  \(\text{\textsuperscript{1}}\text{H NMR}: \delta: 7.7 [4H,q], \delta: 7.5 [4H,q].\) |
| B: Quinoline8-thiol modified naphthalene | Additional peaks  
  IR: 3040 cm\(^{-1}\), 2585 cm\(^{-1}\) 680 cm\(^{-1}\)  
  \(\text{\textsuperscript{1}}\text{H NMR}: \delta: 2.99\) |
| C: Quinoline8-thiol modified naphthalene + Mercury (II) | Peaks disappeared  
  IR 2585 cm\(^{-1}\), 680 cm\(^{-1}\)  
  \(\text{\textsuperscript{1}}\text{H NMR}: \delta: 2.99\)  
  Additional peaks  
  IR 439 cm\(^{-1}\) 640 cm\(^{-1}\) |

On comparing the IR spectra of A and B two additional peaks appeared in B at 2585 cm\(^{-1}\) and 680 cm\(^{-1}\) which are characteristics peaks of S-H and C-S bonds. In the proton NMR also, an additional peak appeared at \(\delta: 2.99\). From these spectral studies, it was found that Quinoline-8-thiol is coprecipitated with naphthalene and totally acts as collector. While comparing the IR spectra of B and C two additional peaks are seen in C at 439 cm\(^{-1}\) and 640 cm\(^{-1}\), but the peak present in the spectrum of B at 2585 cm\(^{-1}\) disappears in the case of C. The peak at \(\delta: 2.99\) in the NMR spectrum of B, corresponding to the S-H proton disappears in the spectrum of C. These spectral studies indicate the formation of mercury (II)-quinoline-8-thiol complex. The extra peak in the IR spectrum of C at 439 cm\(^{-1}\) indicates the Hg-S bond and the disappearance of peak at 2585 cm\(^{-1}\) in the IR spectrum the peak at \(\delta: 2.99\) in the NMR spectrum of C indicate the loss of proton while complex formation. The shift in IR frequency from 680 cm\(^{-1}\) (in B) to 640 cm\(^{-1}\) (in C) confirms the complex formation through C-S bond.
2.7 EQUILIBRIUM LOADING OF CHELATING AGENT MODIFIED NAPHTHALENE

This experiment was carried out by equilibrating 0.05 g of quinoline-8-thiol modified naphthalene with 0.5 mg of mercury and filtered through a filter paper. The equilibrium loading of quinoline-8-thiol modified naphthalene was calculated to be 875 µg per g of SPE.

2.8 APPLICATION

2.8.1 Analysis of standard reference materials

The accuracy of the developed preconcentration procedure was tested by analyzing standard hair sample supplied by International Atomic Energy Agency, Vienna, Austria. The hair sample was dissolved in HNO₃-H₂O₂ mixture (3:2) and heated for 30 min at 200°C on a hot plate. The dissolved hair material is cooled and diluted with water. The mercury (II) present in the sample was preconcentrated by using quinoline-8-thiol modified naphthalene by following the procedure described in Section 2.4 and determined by dithizone procedure. The results obtained are shown in Table 2.5, from which it is clear that the amount of mercury (II) obtained in hair sample by the developed method is comparable with the certified values. Furthermore, known amounts of mercury (II) were added to standard reference material before dissolution prior to preconcentration and determination procedure. The recoveries were found to be good, indicating the suitability of the developed procedure for the determination of mercury (II) in hair samples. The flow chart for the analysis of human hair samples is given in Fig.2.6.
Table 2.5 Determination of mercury (II) in hair samples
[Hair (IAEA-086) Standard reference material]

<table>
<thead>
<tr>
<th>Mercury (II) added µg/g of hair sample</th>
<th>Mercury found µg/g</th>
<th>Certified value</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.57 ± 0.01</td>
<td>0.573</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>1.06 ± 0.02</td>
<td>-</td>
<td>98.0 ± 1.5</td>
</tr>
<tr>
<td>1.00</td>
<td>1.56 ± 0.01</td>
<td>-</td>
<td>99.0 ± 0.8</td>
</tr>
</tbody>
</table>

*Average of 3 determinations

Fig. 2.6 Flow chart for the analysis of human hair samples
2.8.2 Analysis of human hair samples

Human hair samples of different age and sex, collected from different cities (Tirupati, Chennai, Madurai) were brought into solution, subjected to preconcentration by quinoline-8-thiol modified naphthalene and subsequent determination by dithizone procedure. The results obtained are shown in Table 2.6, along with the standard deviation for triplicate measurements. Furthermore, the results obtained by SPE enrichment followed by spectrophotometric procedure were compared with standard cold vapour mercury analyzer. The mercury(II) in human hair samples was in the range 0.25-1.60 µg/g which are comparable to values reported in literature, viz. 1.8 (USA), 0.7 (Iraq) and 1.2 (Pakistan) µg/g of mercury.

Table 2.6 Analysis of human hair samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mercury found (µg/g)</th>
<th>Present method*</th>
<th>Hg analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40 ± 0.01</td>
<td>0.60 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.65 ± 0.01</td>
<td>0.60 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.27 ± 0.01</td>
<td>0.25 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.27 ± 0.01</td>
<td>0.25 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.50 ± 0.03</td>
<td>1.60 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.30 ± 0.01</td>
<td>1.40 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.30 ± 0.01</td>
<td>1.40 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.08 ± 0.01</td>
<td>1.00 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.50 ± 0.04</td>
<td>2.60 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.54 ± 0.01</td>
<td>0.50 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.40 ± 0.01</td>
<td>0.40 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.75 ± 0.01</td>
<td>0.80 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.27 ± 0.01</td>
<td>0.80 ± 0.01</td>
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<tr>
<td>15</td>
<td>1.54 ± 0.02</td>
<td>1.40 ± 0.02</td>
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<tr>
<td>16</td>
<td>1.00 ± 0.02</td>
<td>1.00 ± 0.02</td>
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<tr>
<td>17</td>
<td>&lt; 0.1</td>
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<tr>
<td>18</td>
<td>&lt; 0.1</td>
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<tr>
<td>19</td>
<td>&lt; 0.1</td>
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<tr>
<td>20</td>
<td>0.41 ± 0.01</td>
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*Average of three determinations
2.9 EXPERIMENTAL

2.9.1 Apparatus

Absorbance values were measured using Hitachi 220 microprocessor controlled double beam spectrophotometer (Hitachi, Japan). Magna IR-5560 spectrometer (Nicolet, USA) and DPX-300 NMR spectrometer (Bruker Avance, Switzerland) were used for taking IR & NMR spectra. LI-120 digital pH meter (ELICO, India) was used for pH measurements.

A pair of matched 10 mm quartz cuvettes which are cleaned with acid mixture thoroughly and washed with distilled water, was used for the study.

2.9.2 Reagents

1) Standard mercury(II) solution (1000 µg/ml): Prepared by dissolving 0.3385 g of mercury(II) chloride in water and diluted to 250 ml. This solution was standardized by titrating with EDTA. A suitable volume of this solution was diluted to get a 10 µg/ml of working solution of mercury (II) as and when required.

2) Sulphuric acid solution (5.0M): 69.4 ml of AR grade concentrated sulphuric acid was added to 180 ml of distilled water.

3) Acetic acid solution (6.0M): 86.2 ml of glacial acetic acid was diluted to 250 ml.

4) Dithizone solution (0.001% w/v): 0.001 g of dithizone was dissolved in 100 ml of chloroform and stored in dark.

5) Other reagents like naphthalene, quinoline-8-thiol, acetone and other reagents were of analytical reagent grade. Double distilled water was used throughout.
2.9.3 Preparation of quinoline-8-thiol modified naphthalene

Quinoline-8-thiol and naphthalene in the weight ratio of 1:100 was dissolved in minimum amount of acetone. This acetone solution was poured as a fine stream into 500 ml of water with constant stirring at room temperature. The coprecipitated mixture was stirred for 3 h and was allowed to settle for 10 min. It was filtered through a filter paper, placed in a Buchner funnel by suction, washed with water and dried in an oven at 40°C for several hours and then stored in amber coloured bottle and kept in desiccator.

2.10 GENERAL PROCEDURE

2.10.1 Solid phase extraction and determination of mercury(II)

A portion of mercury(II) solution (0.5-50 µg) was diluted to 250 ml and the pH was adjusted to 6.0±1.0 by using dil.HCl or NaOH after the addition of 10 ml of 1.0 M ammonium acetate buffer and transferred to 500 ml beaker. 0.5 g of quinoline-8-thiol modified naphthalene was added to the above solution and stirred for 15 min. The residue obtained after filtration was dissolved in 2 ml acetone and determined by dithizone procedure after adding 2.5 ml each of 5.0M sulphuric acid and 6.0M acetic acid, diluted to 15 ml with chloroform equilibrated water and shaken for 1 min with 5 ml of dithizone in chloroform. The chloroform layer was collected over anhydrous sodium sulphate and the absorbance of mercury-dithizone complex was measured at 500 nm.

2.10.2 Procedure for analysis of hair reference material

1 g of hair sample (IAEA-086) was dissolved in 25 ml of HNO₃-H₂O₂ mixture (3:2) and heated for 30 min at 200°C on hot plate. The solution was cooled and the pH of the solution was brought to 6.0±0.1 with sodium hydroxide after the addition of 10 ml of 1.0 M ammonium acetate buffer and transferred to 500 ml beaker. The preconcentration of mercury(II) on quinoline-8-thiol modified naphthalene and determination by dithizone were carried out as described in “General Procedure” given above. The mercury(II) content was
established by reference to calibration graph prepared by taking known amounts of mercury and determined by dithizone procedure.

2.10.3 Procedure for analysis of human hair samples

Hair samples were collected from males and females of different age, cities and states in India. The sampling protocol and washing procedures were carried out by Ryabukin [26], Assarian and Oberleas [27] and Rao et al [28]. One of the hair samples was dissolved in 25 ml of HNO₃-H₂O₂ mixture (3:2) and heated for 30 min at 200°C on hot plate. The solution was cooled and the pH was brought to 6.0±0.1 with sodium hydroxide after the addition of ammonium acetate buffer and transferred to 500 ml beaker. The preconcentration of mercury(II) onto quinoline-8-thiol modified naphthalene and determination by dithizone were carried out as described in “General Procedure” given above. The mercury(II) content was established by reference to calibration graph prepared by taking known amounts of mercury and determined by dithizone procedure.

2.11 CONCLUSION

The experiments reported in this study reveal the flexibility and reliability of preconcentration of mercury(II) by solid phase extraction in a batch mode and spectrophotometric determination. The limit of detection is lowered (0.001µg/ml) when compared to methyltrioctyl ammonium chloride (D.L=0.13 µg/ml) modified naphthalene. The SPE procedure facilitates a 50 fold enrichment of mercury (II) from dilute solutions. Since the elution is not done here, more number of samples can be analyzed in a short time. The developed preconcentration procedure enables the reliable determination of mercury (II) in hair samples using a simple, low cost and readily available spectrophotometer.
REFERENCES


