A CATALYTIC SPECTROPHOTOMETRIC METHOD FOR THE ANALYTICAL DETERMINATION OF TRACE AMOUNTS OF MERCURY (II) USING 2-HNAINFH

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ABSTRACT
A catalytic method has been developed for the determination of microgram amounts of mercury (II) based on its catalytic effect on the rate of a ligand substitution reaction. The reaction studied involved the substitution of cyanide in hexacyanoferrate (II) by 2-HNAINFH (2-hydroxy 1-napthaldehyde isonicotinoyl hydrazone) and the reaction was monitored spectrophotometrically. The reaction is readily catalyzed by the mercury (II) ions in the pH range 2-5. The orange red solution formed in this study exhibits maximum absorbance at 470 nm in pH-3. The optimum concentration of K₃Fe(CN)₆ and 2-HNAINFH are found to be 2x10⁻³ M and 2-HNAINFH are found to be 2x10⁻³ M and 2-HNAINFH are found to be 2x10⁻³ M and Satisfactory results were obtained for the determination of mercury (II) in the range 0.004-0.048 μg/ml. The effect of foreign ions on the determination was studied. The results which are obtained quite satisfactory. This method promises to become a sensitive spectrophotometric method for the determination of mercury (II).

Key Words: Mercury (II), Catalytic Method, 2HNAINFH, Spectrophotometer

INTRODUCTION
Mercury is highly toxic element and it can be easily absorbed by the animals and human beings (O’Neil, 1995). Due to its high toxic nature, the determination of trace amounts of mercury in water samples is of great importance. Numerous catalytic methods (Petkovic et al., 2007; Qin and Guohua, 2003) for the determination of trace amounts of metals have been reported in the literature. Only few systems have been reported which involve ligand exchange reactions, e.g., hexacyanoferrate (II) is known (Gadia et al., 1978; Mohan 2007) to exchange cyanide ligands with chromomeric organic ligands. Many methods (Fischer, 1993 and Huang, 2002) (Fischer et al., 1993; Huang et al., 2002; Qin et al., 2003; Gadia et al., 1978; Mohan et al., 2007; Fischer et al., 1993; Huang et al., 2002; Svarc et al., 2006; Hosseini et al., 2005; Padmaja et al., 1994; Rajesh et al., 2008 and Resano et al., 2005) for the determination of mercury (II) reported in the literature are very expensive and employ complicated procedure. Kinetic methods are as sensitive as luminescence and activation analysis methods. (Shafawi et al., 1999) The thermal decomposition of hexacyano ferrate (II) is a slow reversible process. Baudish (1927) and Ilmori (1927) proposed that aqueous solution of potassium hexacyanoferrate (II) decomposes slowly to aqua pentacyanoferrate (II) and cyanide ions in the presence of ultraviolet light. The pentacyanoaquo complex produced reacts with aromatic nitroso compounds and produces colored complexes. Salicylaldehyde isonicotinoyl hydrazone was used for the spectrophotometric determination of gallium and indium at pH 6-6.5. In the present method a simple catalytic spectrophotometric method for the determination of trace amounts of mercury (II). It was observed by the authors that, thermal decomposition of hexacyano ferrate (II) is a slow process. When 2-HNAINFH is added to aqueous solution of K₃Fe(CN)₆ in weakly acidic medium faint orange red colour solution is formed. It took about 24 hours for the development of deep orange red colour but addition of small amounts of mercury (II) accelerated the development of deep orange red colour. No such colour was observed when the metal ion was added independently to K₃Fe
(CN)_6 or 2-HNAINH, hence the colour formation was due to the ligand exchange reaction between K_4Fe(CN)_6 and 2-HNAINH in the presence of mercury (II).

MATERIALS AND METHODS
Reagents
All the reagents were analytical grade obtained from Merck. Double distilled water was used for all the experiments. Mercurous chloride solution and potassium ferrocyanide solutions are prepared by dissolving appropriate amounts of respective compounds in double distilled water. 2-HNAINH solution was prepared by dissolving appropriate amount of 2-HNAINH in dimethylformamide. Buffer solution of pH 1.0 – 3.0 was prepared by mixing appropriate quantities of 0.1M hydrochloric acid and 0.2M sodium acetate and that of pH 4.0 – 7.0 was prepared by mixing suitable quantities of 0.2M acetic acid and 0.2M sodium acetate.

Apparatus
Absorbance measurements were made on SHIMADZU 240 UV-Visible Spectrophotometer SL-164. A Metrohm Digital pH meter SWISS make was used for pH measurements.

RESULTS AND DISCUSSION

Procedure
Suitable aliquots of buffer solution, 2-HNAINH solution, Hg (II) solution and distilled water were taken in conical flask. An aliquot of ferrocyanide solution was added from the pipette into the conical flask. A stopwatch was started when the pipette is half-empty. A known volume of the reaction mixture was withdrawn from the conical flask and absorbance was measured at known intervals of time (5 minutes) at 470 nm.

Kinetic Procedure Initials Rate Method
Initials rate method described in present method the stock solutions involved in the study are thermo stated at the desired temperature for about half an hour. Then appropriate quantities are mixed in the sequence-buffer (40%), dimethyl formamide (20%) as solubuliser, mercury (II), 2HAINNH and K_4Fe (CN)_6 solutions. A stop watch is started when the pipette delivering K_4Fe (CN)_6 in to the reaction mixture is half empty. The solution is shaken well and immediately transferred in to the cuvette. The cuvette is placed in the temperature controlled compartment of the spectrophotometer and the absorbance measured at 470 nm at definite intervals of time against hexacyanoferriate (II) solution as the blank. The initial rates are calculated from the absorbance –time curve using the plane mirror method proposed by Latashaw.

Absorption Spectra
The absorption spectra of the following solutions against buffer blank are recorded to arrive at an optimum wavelength for the absorbance measurements.

Solution A:
4ml of buffer solution (pH3) + 1 ml of DMF + 1ml of 2HAINNH (2x10\(^{-3}\)M) + distilled water = 10ml.

Solution B:
4 ml of buffer solution (pH 3) + 1 ml of DMF+0.5 ml of K_4Fe (CN)_6(2x10\(^{-3}\)M) +distilled water =10ml.

Solution C:
4 ml buffer solution (pH 3)+1 ml of DMF +1ml of 2HAINNH (2x10\(^{-3}\)M) +0.5 ml of K_4Fe (CN)_6 (2x10\(^{-3}\) M) + distilled water = 10 ml.

The spectra of solution A, B and C thus obtained are presented in the Figure 1. It is clear from the figure that the solution C has absorption maximum at 470 nm. At this wavelength solution A has at least zero absorbance and solution B has negligible absorbance. Hence \(\lambda\) max is fixed at 470 nm and potassium ferrocyanate (II) chosen the blank for further studies.

Effect of pH
The Experimental solutions containing hexacyanoferriate (II) (2x10\(^{-3}\)M), 2HAINNH (2x10\(^{-4}\)M) and mercury (II) (1x10\(^{-7}\)M) are prepared using the buffer solutions of desired pH. 20% (v/v) DMF is
maintained. The initial rates are determined at 30°C. The results suggest that the initial rate is maximum buffer solution of pH 3. The low rate in pH s 1 and 2 may due to the protonation and the decrease at higher pH s may be due to the depletion in the concentration of Hg²⁺ because of the hydrolytic precipitation as hydroxide. pH 3 is chosen for further studies. The results are presented in Figure 1.

**Effect of 2 HNAINH Concentrations**

The ferrocyanide concentration and mercury (II) concentration fixed at 2x10⁻³ M and 1x10⁻⁷ M respectively and the concentration of 2HNAINH were varied from 1x10⁻⁴ to 7x10⁻⁴ M. It is clear from the graph that the plot is linear up to 4x10⁻⁴ M and then remains unchanged. Hence an optimum concentration of 2HNAINH is fixed at 2x10⁻⁴ M for further studies. The linear plot of initial rate Vs 2 HNAINH in Figure 2.

**Effect of Ferrocyanide Concentration**

Experimental solutions are prepared in a set of 10 ml standard flasks using buffer solution of pH 3 and maintaining 20% DMF. The concentrations of 2HNAINH and smercury (II) are fixed at 2x10⁻⁴ M and 1x10⁻⁷ M respectively. To this known aliquots of potassium hexacyanoferrate (II) are added and the initial rates determined at 30°C .The results are presented in the Figure 3. A graph is drawn between the initial rate and the concentration of K₄Fe(CN)₆. The figure suggest that the rate increases rapidly up to 4x10⁻³ M, but at higher concentrations rate increases is slow and does not become constant. Therefore further experiments are carried at optimum concentrations of 2x10⁻³ M.
**Figure 3: Effect of Ferrocyanide concentration**

**Determination of Hg2+**

Fixing the pH at 3 and maintaining the concentrations of K₄Fe(CN)₆ and 2HNAINH at 2x10⁻³ and 2x10⁻⁴ M respectively, the concentration of HgCl₂ solution is varied in the range 0.2x10⁻⁷ M to 2.8x10⁻⁷ M. The reaction is followed at 30 °C and the initial rates calculated. The results are presented in Table 1. A calibration curve drawn between the amounts of mercury added and the initial rate is shown in Figure 4.

**Figure 4: Effect of mercury (II) µg ml⁻¹**

This curve suggests that mercury (II) can be determined in the range (0.004 - 0.048 µg.ml⁻¹).

<table>
<thead>
<tr>
<th>Amount of Mercury (II)</th>
<th>Initial Rate x 10⁻⁴ Sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>10.20</td>
</tr>
<tr>
<td>0.008</td>
<td>11.40</td>
</tr>
<tr>
<td>0.016</td>
<td>13.20</td>
</tr>
<tr>
<td>0.020</td>
<td>13.90</td>
</tr>
<tr>
<td>0.028</td>
<td>15.60</td>
</tr>
<tr>
<td>0.036</td>
<td>17.00</td>
</tr>
<tr>
<td>0.040</td>
<td>18.41</td>
</tr>
<tr>
<td>0.048</td>
<td>20.80</td>
</tr>
<tr>
<td>0.056</td>
<td>21.80</td>
</tr>
</tbody>
</table>

The intercept obtained by exploration the straight line gives the rate of the unanalysed reaction. The decline in the rate at higher concentrations of mercury (II) may be due to the formation of a binary
adduct $[\text{Fe (CN)}_6\text{HgCl}_2]$, as the adduct is known to decrease the rate of the forward reaction. The existence of a similar complex between $\text{Fe (CN)}_6^{4-}$ and $\text{Hg (CN)}_2$ is reported by Beck et al.

**Effect of Temperature**

The concentrations of $\text{K}_4\text{Fe (CN)}_6$, $2\text{HNAINH}$, and $\text{HgCl}_2$ are fixed at $2 \times 10^{-3}$ M, $2 \times 10^{-4}$ M, and $1 \times 10^{-7}$ M respectively and the initial rates determined at $20^\circ C$, $25^\circ C$, $30^\circ C$, and $35^\circ C$. Higher temperatures are not attempted for fear of probable decomposition of the orange red complex. The results indicate that the initial rate increases with temperature. As the reaction process at a measurable rate at $30^\circ C$. Further studies are carried out at the laboratory temperature $30^\circ C$.

**Effect of Foreign Ions**

In order to explore the analytical applicability of this method, the effect of diverse ions substances on the determination of mercury (II) is studied. Keeping the pH at 3 and the concentrations of $\text{K}_4\text{Fe(CN)}_6$, $2\text{HNAINH}$ and $\text{HgCl}_2$ at $2 \times 10^{-3}$, $2 \times 10^{-4}$ and $1 \times 10^{-7}$ M respectively, the effect of diverse substances on the initial rate is studied at $30^\circ C$. The error in the initial rate of the order of $\pm 2\%$ is taken as the tolerance limit. The results are presented in the Table 2.

<table>
<thead>
<tr>
<th>Diverse Substances</th>
<th>Tolerance Limit µg .ml$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>20</td>
</tr>
<tr>
<td>Sulphate</td>
<td>16</td>
</tr>
<tr>
<td>Phosphate</td>
<td>12</td>
</tr>
<tr>
<td>Chloride</td>
<td>10</td>
</tr>
<tr>
<td>Thicyanate</td>
<td>10</td>
</tr>
<tr>
<td>Thiosulphate</td>
<td>08</td>
</tr>
<tr>
<td>Fluoride</td>
<td>01</td>
</tr>
<tr>
<td>Magnesium(II)</td>
<td>12</td>
</tr>
<tr>
<td>Calcium(II)</td>
<td>08</td>
</tr>
<tr>
<td>Barium(II)</td>
<td>08</td>
</tr>
<tr>
<td>Cobalt(II)</td>
<td>03</td>
</tr>
<tr>
<td>Aluminium(II)</td>
<td>02</td>
</tr>
<tr>
<td>Nickel(II)</td>
<td>01</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

During the course of investigation it is observed that hexacyanoferrate (II) forms an orange red complex with $2\text{HNAINH}$ in buffer solution of pH 3 which is a slow reaction. This reaction is due to the replacement of cyanide in hexacyanoferrate (II) by isonicotinoyl hydrazones of carbonyl compounds and this is readily catalysed by the mercury (II) ions in the pH range 2-5.

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Research Article


