CHAPTER II

SYNTHESIS OF CHELATING AGENTS
AND
SAMPLE PREPARATION

ABSTRACT

Hydroxamic acids have been used as a chelating agents for the trace determination of heavy metals. These acids were synthesised by reacting hydroxylamine and acid chloride at lower temperature in the suspension of sodium bicarbonate in the ethereal media. These acids were characterised by elemental analysis, mp, ir and uv spectra.

A detail procedure for the environmental sample is described.
INTRODUCTION

The special interest in the search of specific analytical reagents, has led to the use of a large number of organic ligands for the complex formation with metal ions. The organic reagents by their ease of substitution afford reagents of desired analytical properties.

Hydroxamic acids having the bidentate functional grouping, (I), fulfill the basic requirement of complex formation with the metal ions and therefore form an important formily of chelating agents.

\[
\begin{align*}
- \text{N} & - \text{OH} \\
| & \\
- \text{C} & - \text{O}
\end{align*}
\]

(I)

The hydroxamic acids were synthesised based on the procedure of Agrawal et al (1-5). Generally the preparations are made by reacting hydroxylamine with acid chloride at low temperature in diethyl ether solution containing aqueous suspensions of sodium bicarbonate.

In the present investigation the benzohydroxamic acid (II), BHA, and N-phenylbenzohydroxamic acid (III), PBHA, were used for the trace determination of metal ions
in the environment.

The environmental samples collection and preparation were made by standard methods (6,7).
EXPERIMENTAL

CHEMICALS

All the chemicals used were of AnalaR or G.R. grade of B.D.H. and E. Merck unless otherwise described.

N-PHENYLHYDROXYLAMINE

It was freshly prepared as described by Vogel (8) by the reduction of nitrobenzene with zinc dust and ammonium chloride from aqueous media and recrystallised from a mixture of benzene and petroleum ether.

PREPARATION OF N-PHENYL BENZOHYDROXAMIC ACID (PBHA)

It was synthesised by the modified procedure of Agrawal et al (1-5).

0.12 mole of phenylhydroxylamine in 30-40 ml of diethyl ether, a suspension of sodium bicarbonate (0.15-0.2 mole) and 15 ml of water was mixed together and the mixture was stirred mechanically. The contents were cooled externally to 0°C or lower. The 0.1 mole of benzoyl chloride in 100 ml of diethyl ether was added dropwise during the course of about an hr. The stirring was continued for another 30 min and the temperature was maintained 0°C or lower, most of the compound was
precipitated as white solid. The ether layer was separated and removed under vacuum. The yellow residue was mixed with a bulk of white precipitated solid and triturated with saturated solution of sodium bicarbonate in a glass mortar for about 15 min to remove acidic impurities if any. The N-phenylbenzohydroxamic acid was filtered, washed, dried and recrystallised from a mixture of benzene and petroleum ether (60-80°C), mp 121° reported 122°C (9). Generally two to three crystallizations gave a fairly pure product.

**BENZOHYDROXAMIC ACID (4)**

Into a 500-ml flask was placed 6.95 g of hydroxylamine hydrochloride in 40 ml of ethyl alcohol and 18.8 g of sodium bicarbonate in 15 ml of water was added. Next, 14.0 g of benzoyl chloride in 30 ml of ethyl alcohol was added in a period of 30 min with constant stirring. The reaction mixture was cooled to 0°C and the stirring was continued for 15 min more. The liquid layer was separated and mixed with 20 ml of petroleum ether. Any solid product thus obtained was separated and the alcoholic mixture was distilled under vacuum. The white solid benzohydroxamic acid thus obtained was combined with the bulk product and crystallised from ethyl acetate, mp, 128°, reported 128° (5).
SAMPLING

The method of sampling is essentially the same as described by WHO (6).

SAMPLE PREPARATIONS

WATER SAMPLE

The collected water samples were filtered through the Whatman filter paper No. 542 and used as such for trace heavy metals determination.

PLANT AND SOIL SAMPLES

Depending upon the concentration of heavy metals in plants or soils, about 1-10 g of samples were digested with excess of hydrochloric and 10 ml perchloric acids. The filtrate was evaporated and diluted to 100 ml with 0.01 M HCl. The appropriate aliquot of this solution was used for determination of trace metals.
RESULTS AND DISCUSSION

The physical properties of benzohydroxamic acid (BHA) and N-phenylbenzohydroxamic acid (PBHA) are given in Table 1. These acids are stable to heat, light and air. The BHA is freely soluble in water. While PBHA is sparingly soluble in water but readily soluble in ethyl alcohol, benzene, chloroform, diethyl ether, dioxan and carbon tetrachloride.

These acids were characterised by the IR and UV spectra (Table 1) and ionization constants, pKa, (Table 2).

The thermodynamic ionization constants were determined at different mole fraction of dioxan (0-70\%) at 25° and 35° and values are given in Table 2.

The pKa have been determined by a pH titration method (9-12,13) using Elico digital pH meter with glass and calomel electrode.

These acids were synthesised for the plausible analytical applications and determination of trace heavy metals in the environment, Chapter III.
### TABLE 1
Preparation and Properties of Hydroxamic Acids

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>Benzohydroxamic acid (BHA)</th>
<th>N-Phenylbenzohydroxamic acid (PBHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>mp</td>
<td>128°C</td>
<td>121°C</td>
</tr>
<tr>
<td>II</td>
<td>UV Spectra (10)</td>
<td>(\lambda_{\text{max}})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95% ethanol</td>
<td>225</td>
<td>268</td>
</tr>
<tr>
<td></td>
<td>0.1 N HCl</td>
<td>225</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>0.1 N NaOH</td>
<td>268</td>
<td>285</td>
</tr>
<tr>
<td>III</td>
<td>IR Spectra (4,11)</td>
<td>Frequencies, cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\nu) O-H</td>
<td>2770</td>
<td>3175</td>
</tr>
<tr>
<td></td>
<td>(\nu) C=O</td>
<td>1640</td>
<td>1635</td>
</tr>
<tr>
<td></td>
<td>(\nu) N-O</td>
<td>-</td>
<td>909</td>
</tr>
</tbody>
</table>
**TABLE 2**

Thermodynamic Ionization Constants of BHA and PBHA

<table>
<thead>
<tr>
<th>Volume % dioxan</th>
<th>pKa</th>
<th></th>
<th>BHA</th>
<th></th>
<th>PBHA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°</td>
<td>35°</td>
<td>25°</td>
<td>35°</td>
<td>25°</td>
<td>35°</td>
</tr>
<tr>
<td>0</td>
<td>8.91</td>
<td>8.79</td>
<td>8.45</td>
<td>8.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.17</td>
<td>9.02</td>
<td>8.85</td>
<td>8.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>9.79</td>
<td>9.64</td>
<td>9.76</td>
<td>9.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>10.14</td>
<td>10.03</td>
<td>10.30</td>
<td>10.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>10.41</td>
<td>10.26</td>
<td>10.63</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>10.69</td>
<td>10.57</td>
<td>11.04</td>
<td>10.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


REFERENCES
