LETTERS TO THE EDITOR

ANALYTICAL APPLICATIONS OF 5-ETHYL RESACETOPHENONE OXIME (5-ERAPO)

Gravimetric Determination of Copper

5-ETHYL resacetophenone oxime (5-ERAPO) has been found to be a suitable chelating agent for gravimetric determination of copper. The reagent reacts quantitatively with Cu(II) in the pH range 3·5 to 9·0 giving an insoluble metal complex. The buff coloured copper complex can directly be weighed as Cu(C\textsubscript{10}H\textsubscript{12}O\textsubscript{3}N\textsubscript{2}) after drying at 110° C. The error being less than ±0·3%. The reagent gives pale green precipitate with Ni(II) at pH 5·0, orange yellow precipitate with Co(II) at pH 6·5 and violet colour with Fe(III) at pH 2·5 to 4·5. The interference due to several ions such as Ca(II), Ba(II), Sr(II), Mg(II), Ni(II), Co(II), Zn(II), Al(III) has been avoided by working at controlled pH and by using suitable masking agent. The accuracy in the above case is ±0·7%.

The reagent\textsuperscript{1} was prepared as follows:

4-Ethyl resorcinol (7·5 gm), obtained by the Clemmensen's reduction of resacetophenone, was heated with fused zinc chloride (20 gm) in glacial acetic acid (30 ml). The reaction mixture was boiled and then cooled to room temperature. This reaction mixture was cooled with ice after the addition of 100 ml of cold 50% HCl. The product 5-ethyl resacetophenone (5·2 gm) was crystallised from hot benzene (M.P. 119° C), its oxime was prepared by the usual method and crystallised from hot water (M.P. 141° C).

The copper bischelate Cu(C\textsubscript{10}H\textsubscript{12}O\textsubscript{3}N\textsubscript{2}) (Cu calculated 14·06%, found 13·92%) with the reagent precipitated at pH 3·5 is buff coloured and is insoluble in water, 40% ethanol, ether and dilute acetic acid; but it is soluble in chloroform and ethanol.

Procedure for determination of Cu(II).—An aliquot standard solution of Cu(II) containing 15 to 63 mg metal was diluted to 200 ml and pH was adjusted using acetate buffer. The solution was warmed to 60° and 1·0% ethanolic solution of the reagent was added with constant stirring till it was 10% excess over the calculated amount. The precipitate was digested at about 60° and allowed to stand for about 30 min. It was filtered through a sintered glass crucible (G4), washed with 40% ethanol to remove excess reagent, dried at 110° to 120° C to constant weight and finally weighed as Cu(C\textsubscript{10}H\textsubscript{12}O\textsubscript{3}N\textsubscript{2}). The gravimetric factor (copper/copper complex) is 0·1407. The results are given in Table I.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Determination of copper</td>
</tr>
<tr>
<td>Cu(I) mg (taken)</td>
</tr>
<tr>
<td>7·85</td>
</tr>
<tr>
<td>15·71</td>
</tr>
<tr>
<td>31·43</td>
</tr>
<tr>
<td>47·14</td>
</tr>
<tr>
<td>62·86</td>
</tr>
</tbody>
</table>

Determination of copper in presence of other ions.

The pH range at which the precipitation of Ni(II) and Co(II) takes place is higher than that for the precipitation of Cu(II). It was therefore possible to determine Cu(II), (30 mg) at pH 3·5 in the presence of an equal amount of Ni (% error 0·2) and Co (% error 0·7). Zn(II), Mg(II), Ba(II), Ca(II), Sr(II) were found to give no colour nor an insoluble chelate. Hence copper could be determined in presence of these ions with a maximum error of 0·7%. Ferric (III) interferes during the precipitation of copper (II); however the determination was carried out sequestering Fe(III) by potassium citrate.

Chemistry Department, N. D. NAIK.
S.V.R. College of Engineering, H. B. NAIK.\textsuperscript{6}
Surat 395001, July 22, 1974. C. M. DESAL.\textsuperscript{**}

\textsuperscript{6} Present address : Chemistry Department, Gujarard College, Ahmedabad, 380006.
\textsuperscript{**} Present address : P.T. Sarvajank College of Science, Surat 395001.


REACTION ON BIS-FORMAMIDINE DISULPHIDE WITH INDOLE

With a view to extending the reaction\textsuperscript{1} of bis-formamidine disulphide dihydrobromide I, to reactive aromatic systems other than phenols, the reaction of I with indole was investigated. Indole 1·2 g was heated with 3·1 g of I at 60° for 30 minutes. The reaction mixture was cooled, triturated with water and filtered when a dry white hydrobromide 1·9 g (70%) was obtained, crystals from warm, dil. HBr, m.p. 217-219° (decomp.) (Found : C, 40·12; H, 4·08; N, 15·11%). Required for C\textsubscript{9}H\textsubscript{10}N\textsubscript{3}SBr C, 39·70; H, 3·67; N, 15·44%).
The n.m.r. spectrum of the hydrobromide in D₂O n.m.r. frequencies showed multiplets as expected, in 7.3–7.9 δ region for all the aromatic protons of indole, the other protons attached to nitrogen showing no peaks due to exchange with D₂O.

The most probable site in indole for attack of the sulphenium ion, δS= C−NH₂, is the 3 position, δ\\overset{\text{NH₂}}{\text{Br}}
resulting in the formation of the hydrobromide II. That the hydrobromide was not a disulphide of the type III could be seen by its lack of reactivity aq. KI and aq. H₂S solution.

\[
\begin{align*}
\text{HV} & \text{N-C-S} \\
\text{Br-H₂N} & \text{NH}_2 \\
1 & \text{II}
\end{align*}
\]

The II on treatment with cold dil. alkali immediately precipitated a pale yellow solid which darkened on exposure to air. The sulphides of the type IV are known to decompose in alkaline solution to thiols, which slowly get oxidised to disulphides. The dark coloured solid from II had m.p. 90–110°; the thiol from the corresponding hydriodide of II obtained under nitrogen atmosphere is reported to melt at 99–100°. The dark solid (the m.p. of which kept rising on keeping) on shaking with H₂O₂ for an hour, gave a white solid; crystallised from dil. ethanol, m.p. 214–217°; reported m.p. for disulphide VI is 218–220°.

\[
\begin{align*}
\text{IV} & \text{V} \\
\text{VI} & \text{O}
\end{align*}
\]

The II on Schotten Baumann benzylation gave a pale yellow crystalline benzoate V, m.p. 144–145° (from ethanol), (Found S, 12.03; calc. for C₁₅H₁₁O₇S 12.64%). The reported m.p. for the benzoate V is 142–144°. That the sulphur was linked at the 3 position of the indole was demonstrated by the earlier workers.

Thanks of the author are due to the authorities of Banaras Hindu University for providing the facilities and to the C.S.I.R. for the award of Paul Officership (1971–73).