Synthesis of 2-[4-Antipyriylazo] Orcinol as a New Sensitive Reagent for Determination of Cu (II) in Fly ash by Spectrophotometric Method

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Abstract-- A spectrophotometric method was developed for the determination of Cu(II). The method was based on the formation of Fe (II), Ni(II) 2-[4-antipyylazo ] orcinol(APAO) complex. The complex have been characterized by spectroscopic methods such as UV-Visible, FT-IR, molar conductivity measurements, melting points. The maximum absorbance of complex is at 474 nm with molar absorptivity of (0.55x10^4) L.mol^{-1}.cm^{-1} of Cu(II). Mole ratio of the complex which is formed between Cu(II) with APAO is 1:1 which was calculated by both the mole ratio and continuous variation methods. The absorbance of the complex obeys Beer’s law in the concentration range of (0.1-3.0) μg.ml for Cu(II). The stability constant of the complex under optimized conditions and at room temperature was (0.13x10^7) L.mol^{-1} for Cu(II). This procedure can be carried out in the presence of many cations and anions in the presence or absence of the masking agents. The method was successfully applied to the determination of Cu(II) ion in analytical and fly ash samples.

Index Term- 2-(4-antipyriylazo ) orcinol ,Copper (II) determination ,spectrophotometry.

Introduction

Pyrazolonesazo versatile heterocyclic, which have very important application in both chemistry and biology due to the great flexibility and diverse structural aspects, a wide range of pyrazolone have been synthesized and their complexation behavior studied [1-5]. Moreover, pyrazoles attached to a sulphanilamido moiety through an azo linkage have been reported to exhibit biological activity [6]. It is known that pyrazoloneazo compounds are widely used because of their very good chelatogenic characteristics. The activity of Pyrazoloneazo is thought to be due to their power of chelation with traces of metal ions present in biological systems [7-12]. Determination of Copper (II) by various methods has been developed. Many of these methods require complicated and expensive instruments, therefore, development of Copper (II) in different samples seem desirable [13-15]. The aim of the present work is to develop an easy, rapid method for the determination of copper (II). The method is based on the reaction of -[(4-antipyyl azo )] orcinol(APAO), with forms coloured complexes which forms coloured complex with Cu(II) ion.

Experimental

I/ Preparation of the reagent (APAO)

The reagent was prepared by coupling Orcinol with diazotate 4-amino antipyrine in alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g from 4-amino antipyrine in 25 ml of ethanol and concentrated hydrochloric acid with 6 ml of distilled water and adding sodium nitrite solution drop wise at (0-5 C°). Orcinol 1 g was dissolved in 25 ml of ethanol and 50 ml of sodium hydoxide were added at (0-5 C°). The mixture was left to stand overnight. The precipitate was filtered off and recrystallized from ethanol [16]. Schem1.
II/Preparation of Cupper (II) complex

The complex was prepared by stoichiometric amount from ligand in 100 mL of ethanol then added drop wise with stirring to a stoichiometric amount 1:1 for Cupper salt in 100 ml distilled water. The solid product thus formed off, washed with ethanol and dried.

**Apparatus**

Spectrophotometric measurement were made with UV–visible T80 double beam spectrophotometer using 1.00 cm glass cells. Vibrational spectra were recorded on Test scan Shimadzu FT.1R 8000 series. Measurements of pH were made using Inolab pH–meter WTW 720 equipped with a glass–saturated calomel combined electrode. Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus 9300. Conductivity was measured in DMSO (10^5) solution with an Inolab conductivity model–WTW 720.

**Reagents**

All chemicals used were of analytical grades.

**Cupper (II) stock solution (100 µg . ml^-1)**

Prepared by dissolving 0.042 g of Cupper chloride in 200 ml of distilled water, working standard of Cu (II) solutions were prepared by simple dilution of the appropriate volume of the standard Cu (II) solution (100 µg . ml^-1) with distilled water.

**2(4antipyriyl azo)Orcinol (1 mM )**

0.067 g of reagent was dissolved in 200 ml of ethanol.

**Foreign ion solutions ( 10 µg . ml^-1 )**

These solutions were prepared by dissolved an amount of the compound in distilled water completing the volume in a volumetric flask.

General Procedure

In to a series of 10 ml calibrated flask, transfer increasing volumes of Cu(II) working solution 10 ppm to cover the range of calibration curve, add 3 ml of 1mM of (APAO) solution and pH was adjusted to 8.0. The complexes formed were solubilized in water and diluted up to 10 ml in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition but Cu(II) no.

**RESULTS AND DISCUSSION**

Properties of (APAO) and its metal chelate APAO is a tridentate with coordination of azo group nitrogen, hydroxyl group and carbonyl group; it has the following structure:
Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates. APAO and its metal chelates can be easily solubilized in an aqueous solution.

**Spectra**

The results of this investigation indicated that the reactions of Cu(II) with 2(4-pyrazolon azo) orcinol yields highly soluble colored complexes which can be utilized as a suitable assay procedure for determination of Cu(II). The electronic absorption of APAO and its complex in ethanol have been recorded in the wavelength range (190 – 800) nm. This colored complex has a maximum absorption at 474 nm for Cu(II), the blank at this wavelength shows zero absorbance Fig. 1.

![Absorption spectra of [Cu (II) + APAO] treated as described under procedure and against a reagent blank and reagent blank against ethanol.](image)

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized.

To establish the optimum condition (stability of the product from the reaction of Copper (II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (4.0-10.0) was studied. Only pH 8.0 and 6.0 was found to be optimum for Cu(II). Acid and alkaline results in low sensitivity and was not stable for Cu(II). pH change on the electronic absorption spectra of the complex was studied by adding a small amount of 0.05 M HCl and 0.05 M of NaOH. The UV-Visible spectra of complex gives the band centered at 474 nm for Cu(II). The bands appearing in the range of 240-311 nm for Cu(II) is attributed to π→π* transition. The other band observed in the region of 474 nm is attributed to n→π* electronic transition [17-19] for Cu(II) Fig. 2 Table I.

![Effect of pH on complex Cu-APAO](image)
Table I
Analytical characteristics of Cu-APAO complex.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Co (II) – complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maximum (nm)</td>
<td>474</td>
</tr>
<tr>
<td>Beer’s law range (ppm)</td>
<td>(0.1 – 3.0)</td>
</tr>
<tr>
<td>pH range</td>
<td>(6.0–8.0)</td>
</tr>
<tr>
<td>Sandell sensitivity µg . cm²</td>
<td>0.011</td>
</tr>
<tr>
<td>Molar absorptivity (L. mol⁻¹. cm⁻¹)</td>
<td>0.55 X 10⁴</td>
</tr>
<tr>
<td>Melting point for reagent</td>
<td>(233 – 235)C⁰</td>
</tr>
<tr>
<td>Melting point for Cu (II) – complex</td>
<td>(238.5– 240.5) C⁰</td>
</tr>
</tbody>
</table>

Effect of (APAO) concentration

Various concentration of 2-(4- antipyriyl azo) Orcinol was added to fixed concentration of Cu (II) .3 ml of 1 mM (APAO) solution was sufficient and gave minimum blank value was increased causing a decrease in the absorbance of the sample. Therefore3 ml of 1 mM of APAO was used in all subsequent experiment Fig. 3.
Effect of reaction time
The colour intensity reached a maximum after the Cu (II) has been reached immediately with APAO and became stable after one minute, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for at least 24 hours Fig 4.

![Fig 4. Effect of time on complex of Cu[APAO]Cl](image)

Effect of temperature
The effect of temperature on the colour intensity of the product was studied. In practice, the same absorbance was obtained when the colour was developed at (10 – 60) °C, but when the volumetric flask were placed in a water bath at 70 °C a loss in colour intensity and stability were observed, therefore it is recommended that the colour reaction should be carried out at room temperature for complex Fig 5.

![Fig 5. Effect of temperatures on complex Cu[APAO]Cl](image)

Order of addition of reagents
To obtain the optimum results, the order of addition of materials should be followed as give by the procedure, otherwise a loss in stability are observed.

Calibration graph
At optimum conations ,a linear calibration graphs for Cu(II) was obtained ,that Beers low is obeyed over the concentration range of (0.1-3.0 ppm) with a correlation coefficient ( R^2 = 0.9959) .Since the coloured complex is stable for 24 hrs , the method can be applied to large series of samples . The molar absorptivity and sandell’ sensitivity are given in Table.I.

Composition of the complex
The composition of complex was studied in the excess of reagent solution by the mole-ratio and Job’s methods [20,21] Fig 6,7. A break at a 1:1 (M:L) mole ratio suggested the formation of complex where M= Cu(II) and L= APAO under the given condition.

![Fig 6. Mole-ratio method for Cu[APAO] complex](image)
Conductivity measurements

The solubility of the complexes in dimethylsulfoxide and ethanol permitted of the molar conductivity of 10$^{-3}$ M solution at 25 °C and by comparison, the electrolytic nature for complex. The low values of the molar conductance data listed in Table II indicate that the complex is electrolytes.

Interferences

The effect of diverse ions in the determination metal ion was studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. The metal ion can be determined in the presence of a 10 or more fold excess of cation and anion Table. III. In the experiment, a certain amount of standard Cu (II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. It is found some of studied ions interfere seriously. However, their interferences are masked efficiently by addition 1.0ml or excess of 0.1 M of Na$_2$HPO$_4$, Oxalic Acid, Thiourea.

FT.IR of reagent and it’s complex

The FT.IR of the free ligand and it’s metal chelate were carried out in the (400-4000) cm$^{-1}$ range . The IR bands of the (APAO) and its Cu (II) complex with their probable assignment are given in Table. IV. The IR spectrum of ligand shows a broad band at 3435 cm$^{-1}$, which can be attributed to the OH group. However, the υ(N=N) stretching band in the free ligand is observed at 1506 cm$^{-1}$. This band is shifted to lower with low intensity at 1444 cm$^{-1}$ upon complexation suggesting chelation via the (M-N)$^{2-}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>v (OH)</th>
<th>v (C-H)</th>
<th>v (N=N)</th>
<th>v (C=O)</th>
<th>v (M-O)</th>
<th>v (M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>3435</td>
<td>3090</td>
<td>1506</td>
<td>1693</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[Cu(APAO)]H$_2$O</td>
<td>3412</td>
<td>3050</td>
<td>1444</td>
<td>1687</td>
<td>505</td>
<td>420</td>
</tr>
</tbody>
</table>

S: sharp ; m: medium ; w: weak
On the basis of the FT.IR, stoichiometric, and elemental analysis, molar conductivity data the structure of complex can be suggested as the following :–.

Structure of Complex

Applications

1-Determination of Cupper (II) in practical samples

To determine the accuracy and precision of the method, Cupper (II) was determined at two different concentrations with different interferences ions and masked these ions by using masking reagent. The results are shown in Table. V, which indicate satisfactory precision and accuracy could be attained with proposed method.

<table>
<thead>
<tr>
<th>Amount taken of Cu (II) p.p.m</th>
<th>Recovery %</th>
<th>*RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>99.38</td>
<td>1.30</td>
</tr>
<tr>
<td>3.0</td>
<td>98.80</td>
<td>0.94</td>
</tr>
</tbody>
</table>

*For five determinations

2-Determination of Cupper (II) in fly ash samples.

10 g of fly ash dissolved in beaker by 5 ml of concentrated HNO3 and diluted to 25 ml by distilled water and then evaporated to dryness. The residue was dissolved in distilled water and translated to volumetric flask with capacity 100 ml and then the sample ready for UV-Visible spectrophotometric analysis [27].

Table VI

Determination of Cu (II) in fly ash sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Con.of sample μg / g</th>
<th>*R.S.D %</th>
<th>Re . %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>1.63</td>
<td>0.42</td>
<td>99.52</td>
</tr>
</tbody>
</table>

*For five determination

REFERENCES