Picorinaldehyde nicotinoylhydrazone for trace level separation and spectrophotometric determination of copper(II)

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A sensitive method is proposed for extraction and spectrophotometric determination of copper(II) at trace levels using picorinaldehyde nicotinoylhydrazone (PANH) as an analytical reagent. The yellow coloured PANH-Cu(II) complex, extracted into chloroform in the pH range 8.5-10.5, shows maximum absorbance at 380 nm. Beer's law is obeyed over the range 10-300 ng ml⁻¹ of copper(II). The molar absorptivity and the Sandell's sensitivity for copper(II):PANH system has been found to be 5.8 x 10⁴ l mol⁻¹ cm⁻¹ and 1.1 ng cm⁻² respectively. The extracted species has a 1:2 (metal:ligand) stoichiometry. The proposed method is highly sensitive, selective, simple and rapid, and has been applied for accurate determination of copper in alloys and Pharmaceutical samples.

Copper is considered to be the most important metal after iron. Major portion of the world's copper production is utilised by the electrical industries and a large part of the remainder is combined with other appropriate metals to form alloys. Even in human body, copper is essential in small amounts for synthesis of haemoglobin. Deficiency of copper causes diseases like anemia, kinky hair while excess of copper causes jaundice.

Although a number of complexing reagents have been reported for the spectrophotometric determination of copper²⁻⁴, these methods suffer from certain limitations such as narrow pH range, require longer extraction time, have lower sensitivity and molar absorptivity and show significant interference from foreign ions.⁵ Picorinaldehyde nicotinoylhydrazone (PANH) is proposed by us for trace levels determination of copper(II). The method herein is superior, simple, rapid and free from the many limitations in the methods reported above. The method is also comparable with several good spectrophotometric methods.⁶-⁹ The method has been applied for analysis of copper in pharmaceuticals and alloy samples.

Experimental

The absorbance measurements were carried out on a Shimadzu 160/A UV-visible spectrophotometer and atomic absorption spectrophotometer (GBC 932 AA, Australia). The pH measurements were carried out on a Equip-Tronics digital pH-meter (model EQ-610) with a combined glass electrode assembly. The stock solution of copper(II) (5000 μg ml⁻¹) was prepared by dissolving CuSO₄·5H₂O (4.911 g, Qualigens 99%) in doubly distilled water containing 2 ml of conc. H₂SO₄. The solution was diluted to 250 ml with doubly distilled water and standardised by benzoin-α-oxime method.¹⁰ The reagent (PANH) was synthesised as per the method reported in literature.¹¹ Stock solution of the reagent (0.05 %) was prepared by dissolving PANH (0.05 gm) in 10% ethanol. The buffer solution of pH 9.0 was prepared by using 0.1 N NH₄OH and 0.1 N HCl solution. Solutions of other cations and anions were prepared by dissolving their AR grade salts in doubly distilled water with a few drops of suitable acid. Synthetic mixtures were prepared by using standard solutions of copper and of desired metal ions. Analytical grade chemicals were used unless otherwise stated. Doubly distilled water was used throughout the experimental work.

General procedure

To an aliquot of Cu(II) solution, were added 1 ml PANH (0.05%) and 2 ml buffer of pH 9.0. The mixture was diluted to 10 ml with doubly distilled water and equilibrated with 10 ml chloroform for 30 s. The absorbance of the organic layer was measured at 380 nm against a similarly prepared reagent blank. The amount of copper(II) was deduced from the standard calibration curve.

Sample dissolution

In pharmaceutical sample analysis, a single multivitamin tablet was treated with 15 ml of aqua-regia, heated nearly to dryness and then HClO₄ (2 ml) was added to decompose the organic matter. Finally the residue was extracted with 10 ml of 2 M HNO₃, diluted, filtered and made up to the suitable volume.

Different alloy samples were analysed for their copper content. Brass sample (0.2 g) was dissolved in 10 ml of aqua-regia, evaporated to minimum volume,
extracted with 10 ml of 2M HNO₃ and then diluted with doubly distilled water up to the suitable volume.

Solder samples (0.5 g) were dissolved in 15 ml of 6M HNO₃ and boiled. The boiled solution was diluted, filtered and washed. The precipitate of metastannic acid was rejected. Lead was removed as lead sulphate. The filtrate was further diluted to the suitable volume with doubly distilled water.

White metal (0.5 g) sample was dissolved in 15 ml of 6M HNO₃ and heated till boiling. The precipitate of metastannic acid was filtered off, washed and rejected. The filtrate was diluted up to the desired volume with doubly distilled water.

Aluminium chips and pins samples (0.5 g and 0.358 g) were dissolved by heating with 15 ml conc. HCl and 2 ml HNO₃ and evaporated nearly to dryness. The residue formed was extracted in 20 ml of distilled water and dilution was made using doubly distilled water.

Results and discussion
The yellow coloured complex shows absorption maxima at 380 nm against reagent blank, where the absorption of reagent against the pure solvent was found to be negligible. Hence all absorption measurements were carried out at 380 nm against a reagent blank.

Copper(II) was extracted by PANH in chloroform over the pH range of 1.0-11.0. It was found that the complex could be quantitatively extracted in the pH range 8.5-10.5, where the percentage extraction was found to be over 99.9%. Therefore all extractions were carried at pH 9.0. The complex was found to be stable for 23 h.

Various solvents, viz., amyl acetate, ethyl acetate, n-butyl acetate, isoamyl alcohol, toluene, benzene, carbon tetrachloride, methyl isobutyl ketone and chloroform were tried for extraction and it was observed that maximum extraction (99.9%) of copper(II) with PANH was attained with chloroform as the solvent.

The effect of PANH concentration on the extraction of copper(II) was studied. It was observed that 1 ml of 0.025% solution of PANH was sufficient for quantitative extraction of copper(II). Excess of reagent concentration did not affect the extraction. Hence 1 ml of 0.05% reagent was used for further studies.

Table 1—Determination of copper(II) in synthetic mixtures, pharmaceutical and alloys samples

<table>
<thead>
<tr>
<th>Synthetic mixture</th>
<th>Present method</th>
<th>Cert. values</th>
<th>AAS</th>
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<tbody>
<tr>
<td>Cu(2.5) Fe(500) Pd(500)</td>
<td>2.47</td>
<td>-</td>
<td>2.49</td>
</tr>
<tr>
<td>Cu(2.5) Pt(500) Pt(500)</td>
<td>2.49</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>Cu(2.5) Au(200) Ag(200)</td>
<td>2.47</td>
<td>-</td>
<td>2.49</td>
</tr>
<tr>
<td>Cu(2.5) Cr(500) V(500)</td>
<td>2.47</td>
<td>-</td>
<td>2.49</td>
</tr>
<tr>
<td>Cu(2.5) Fe(500) Mo(500)</td>
<td>2.48</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>Pharmaceutical samples</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Supradyn (Nicholas Piramal India Ltd.)</td>
<td>0.862</td>
<td>0.854</td>
<td>0.860</td>
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<tr>
<td>Fersolate CM (Burroughs Wellcome India Ltd.)</td>
<td>0.661</td>
<td>0.658</td>
<td>0.659</td>
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<tr>
<td>Theragran-M (Sarabhai Chemicals)</td>
<td>2.036</td>
<td>2.032</td>
<td>2.034</td>
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<tr>
<td>Alloy samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brass</td>
<td>59.46</td>
<td>59.20</td>
<td>59.30</td>
</tr>
<tr>
<td>White metal</td>
<td>4.02</td>
<td>3.98</td>
<td>4.00</td>
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<tr>
<td>Solder-1</td>
<td>0.12</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>Solder-2</td>
<td>0.19</td>
<td>0.18</td>
<td>0.18</td>
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<tr>
<td>Aluminium chips</td>
<td>4.09</td>
<td>4.06</td>
<td>4.08</td>
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<tr>
<td>Aluminium pins</td>
<td>5.44</td>
<td>5.40</td>
<td>5.42</td>
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</table>

*aAverage of five determinations, b values in µg, c values in mg, d values in %
The colour development was instant, however shaking time was varied from 5 to 120 s after reagent addition. The minimum shaking time required for quantitative extraction of copper(II) was 15 s, while longer extraction time did not affect the percentage extraction. Hence 30 s of shaking time was fixed for further studies.

The absorbance of the extracted species was a linear function of the copper(II) concentration in the range 10-300 ng ml⁻¹. Ringbom’s optimum working range found was 110-280 ng ml⁻¹. The molar absorptivity and Sandell’s sensitivity of the system were found to be $5.8 \times 10^4$ l mol⁻¹ cm⁻¹ and 1.1 ng cm⁻² respectively.

The precision and accuracy of the method was found by the average of ten determinations of 1 ml of stock solution (2.5 μg/ml), which was found to be 2.48 μg with standard deviation 0.07, while deviation from mean at 95% confidence limit was 0.05.

The nature of the complex was determined by slope ratio method. A linear plot of log [D] against log [PANH] at fixed pH, with a slope =2, showed the metal : ligand ratio to be 1:2, i.e., Cu(PANH)₂.

**Effect of diverse ions**

Under the optimum conditions, effect of various cations and anions on extraction of 2.5 μg of copper(II) in 10 ml was studied. The tolerance limit of the diverse ion was set as the amount required to cause an error not greater than ± 2% in the percentage recovery. The tolerance limits for the diverse ion investigated are as follows: F, Cl, Br⁻, I⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, Cl⁻, Br⁻, IO₃⁻, CO₃²⁻, HCO₃⁻, S₂O₇²⁻, S₂O₅²⁻, S₂O₃²⁻, SCN⁻, acetate, citrate, tartrate, oxalate, urea (20 mg each); Li⁺, Na⁺, K⁺, Ca(II), Mg(II), Ag(I), Se(IV) (10 mg each); Al(III), Ba(II), V(V), (7.5 mg each); S₂O₃²⁻, Sb(III), Mo(VI) (5 mg each); Pt(IV), W(VI) (1.5 mg each); Pd(II) (0.7 mg); Cr(III), Fe(III) (0.5 mg each); Au(III) (0.2 mg); U(VI) as UO₂(II) (0.1 mg); CN⁻, EDTA, Bi(III), Sn(II) (0.01 mg each); Hg(II), Pb(II) (5 μg each); Mn(II), Ni(II), Zn(II), Co(II) (5 μg each, each masked with CN⁻).

**Determination of copper in various samples**

The method was tested by applying it for separation and determination of 2.5 μg copper(II) in various synthetic mixtures (Table 1). The method was also applied for estimation of copper in various pharmaceutical and metallurgical samples (Table 1). The results obtained are well in agreement with the results obtained by AAS and the reported values.

**References**