Spectrophotometric determination of copper(II) using cupron in the presence of Brij 35

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An aqueous spectrophotometric method for the estimation of nanogram quantities of copper (II) using cupron in the presence of Brij 35 is developed. The molar absorptivity of the complex is 66000 l mol⁻¹ cm⁻¹ at pH 8 and wavelength 445 nm and the Beer's law is obeyed up to 7 ppm. The method is free from the interferences and has been successfully employed in the analysis of alloys and water.

Most of the sensitive photometric methods reported in literature¹–⁵ for the determination of microquantities of copper are extractive. Attempts were made to solubilise the copper complexes by using surfactants⁶–⁸. Benzoin-α-oxime (cupron) is a specific reagent for copper and is widely used for spot analysis. Copper-cupron complex is water insoluble and is extractable in chloroform.

In the present note, we have developed a process where water insoluble copper-cupron complex is converted into a soluble one in the presence of nonionic surfactant Brij 35. The aqueous complex formed is more sensitive than the extractive one. Copper from the alloys and waters was estimated with accuracy and precision by following the proposed method.

Experimental

All the chemicals and reagents used were of AR grade. A shimadzu UV-vis spectrophotometer Model 240 was used in these studies. A standard solution of copper was prepared by dissolving copper sulphate (0.2497 g) in water and volume was made up to 100 cm³ with deionised water. The resulting solution was standardised by literature method¹. The working solutions were made by appropriate dilutions. A stock solution 0.1% w/v (4.4 × 10⁻³ M) of cupron was prepared in ethanol.

The acetate buffers of varying pH were prepared from the appropriate mixtures of 20% sodium acetate and acetic acid and diluting them with deionised water.

A stock solution of nonionic surfactant Brij 35 was prepared by dissolving Brij 35 (7.8 g) in water and diluting it to 100 cm³ with deionised water. The resultant concentration of the surfactant solution was observed to be 6.5 × 10⁻² M.

Procedure

Extractive method
To a 2 cm³ aliquot of 10⁻⁴ M copper (II) solution (12.7 µg), 25 cm³ of 20% sodium acetate buffer (pH 8) was added. To this, 2 cm³ of 4.4 × 10⁻³ M reagent solution was added and the complex extracted twice with 5 cm³ aliquots of chloroform and the absorbance of the complex was recorded against the reagent blank.

Aqueous method
To a 2 cm³ of 4.4 × 10⁻³ M cupron solution, 5 cm³ acetate buffer (pH 8) was added. To this, 0.5 cm³ of 7.8% Brij 35 and 2 cm³ of 10⁻⁴ M copper(II) solution was added and the volume made up to 10 cm³ with deionised water. The absorption spectrum was recorded against the reagent blank.

Results and discussion

The absorption spectrum of copper-cupron chloroform extractable complex exhibits maxima at 440 and 600 nm with the molar absorptivity of 45500 and 55000 l mol⁻¹ cm⁻¹ respectively. The absorption spectrum of Cu(II)-cupron complex in micellar medium was also recorded and it was observed that a small bathochromic shift in the peak in red region is observed (at λmax 445 and 600 nm). A considerable increase in the sensitivity of the method was observed resulting into a molar absorptivity of 66000 and 12000 l mol⁻¹ cm⁻¹ respectively at 445 and 600 nm. From the spectra obtained for (i) metal, (ii) reagent, (iii) metal + reagent, (iv) metal + surfactant, (v) reagent + surfactant, it was observed that there is no interaction between metal and surfactant or reagent and surfactant. But the enhancement in the sensitivity as well as small bathochromic shifts are the results of the solvent effect on the absorption of Cu(II)-cupron complex.

From the results obtained in the study of effect
of pH on absorption, it was observed that the absorption of the complex is comparatively more pH sensitive at 445 nm. However, isolation of the complexes at pH 6 and 8 and further metal estimation from them supported that both the complexes are identical with metal to ligand ratio of 1:2. Due to higher sensitivity, further measurements were carried out at 445 nm.

In the study of effect of reagent concentration on the development of copper-cupron complex it was observed that 2 cm$^3$ of 4.4 x $10^{-3}$ M reagent was sufficient for the complete complex formation of 12.7 µg of copper in 10 cm$^3$ solution. The complex remained in the solubilised form when surfactant concentration was between 0.3 to 0.8% (w/v). Hence 0.4% concentration of Brij 35 was used throughout the studies. Brij 35 concentration below 0.3% was insufficient for solubilisation of the complex. Use of surfactant concentration of 0.4% and above did not alter the absorbance of the complex.

The complex formation was instantaneous and the absorbance remained stable at least for 6 hr. A calibration curve was constructed in the usual way. Beer’s law was obeyed upto 0-7 µg of copper in 10 cm$^3$ of solution at 445 nm. The linear correlation coefficient of the plot was 0.9985 and the least square equation for absorbance at 445 nm was, $A = 0.1013 \ [\text{Cu(II)} \text{ in µg}] + 0.0615$. The standard deviation was 0.024 µg (n = 5) and relative standard deviation was 2.85%.

Copper-cupron complex was isolated at optimised conditions in the absence of Brij 35. The complex was washed and dried thoroughly and its solubility in water at various temperatures from ambient to 80°C was measured as a function of time. It was observed that even after 24 h at elevated temperatures, solubility of the complex was not considerable. The dissolution of the complex in the presence of different concentrations of Brij 35 was also tried. From the plot of log[Brij 35] vs absorbance it was observed that the dissolution of the complex is a linear function of the log[Brij 35] and not [Brij 35] itself. The linear correlation coefficient was observed to be 0.9982 and the least square equation for absorbance was, $A = 0.0224 \ [\text{Brij 35 M}] + 0.8332$. It was observed that the complex is not soluble if the concentration of the surfactant is below CMC.

The stoichiometry of the complex was determined by Job’s method and mole ratio methods using 10$^{-4}$ M copper and reagent solutions and keeping surfactant concentration constant at 3.2 x $10^{-3}$ M. The results obtained at 445 and 600 nm show the stoichiometry of 1:2 (metal:reagent).

Effect of diverse ions

The interference due to various ions was studied. It was observed that zinc, nickel, cadmium and manganese are tolerated upto 100 fold excess of copper. Silver and iron interfere seriously in the estimation of copper but their interference can be masked by using fluoride. Tin and lead interfere if their concentration is equal to or greater than copper concentration. At lower concentrations, no interference was observed. Thiocyanate, thiosulphate, fluoride and acetate do not interfere even at very high concentrations. Oxalate, ascorbate and citrate can be tolerated in the 1:25 ratio whereas iodide and EDTA interfere seriously.

Analysis of alloys

The alloys BSC Brass 5F (0.1 g) and Gun metal 6F (0.1 g) were taken separately in beakers to which 10-15 cm$^3$ of concentrated HCl and a few drops of concentrated HNO$_3$ were added. The mixture was heated till dissolution and the volume reduced to 5 cm$^3$. The solution was allowed to cool, diluted with dil. HCl, filtered and volume made upto 500 cm$^3$.

An aliquot containing an appropriate amount (25 µg) of copper was taken separately in a beaker and the copper complex was developed as discussed earlier. Zinc, manganese, tin, lead and nickel do not interfere during estimation. The interference due to iron was masked. Brij 35 concentration below 0.3% was insufficient for solubilisation of the complex. Use of surfactant concentration of 0.4% and above did not alter the absorbance of the complex.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition %</th>
<th>Amount of copper %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSC Brass 5F</td>
<td>Zn 24.11, Sn 1.85, Pb 2.52, Fe 0.31, P 0.06, Mn 0.12 and Ni 0.17</td>
<td>70.80 72.37 71.46</td>
</tr>
<tr>
<td>BSC Gun metal</td>
<td>Zn 1.37, Sn 9.22, Pb 1.13, Fe 0.01, P 0.07 and Ni 0.24</td>
<td>87.95 87.91 87.75</td>
</tr>
</tbody>
</table>

*Mean of six determinations
Determination of copper in water

The determination of copper in untreated water from a bore-well and treated tap water was done by following a standard addition method. Linear plots were obtained for standard addition of 20, 30 and 40 μg of copper cm⁻³ to each sample examined. The interfering ions were masked by addition of 2 cm⁻³ of 0.1 M sodium fluoride. The copper concentration observed in untreated water was 25 ng cm⁻³ and that into a tap water (treated) was 7 ng cm⁻³. The results were counter checked by estimating the copper content by atomic absorption spectrometry after pre-concentration.

References
2 Sekin T & Hasegawa Y, Solvent extraction chemistry (Marcel Dekker, New York) 1977.