

Fluorimetric Determination of Copper in Copper Wires using Bis(salicylaldehyde) tetramethylethylenediimine as Complexing Reagent

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Summary: The reagent bis(salicylaldehyde)tetramethylethylenediimine (H_2SA_2Ten) and its copper(II), nickel(II), palladium(II), cobalt(II) and oxovanadium(IV) complexes indicate fluorescence in visible region. The conditions for the fluorimetric determination of metals as metal chelates compounds were optimized. The linear calibrations were obtained in the range of 0-50 $\mu\text{g/ml}$ of a complex in chloroform. Solvent extraction procedure was developed for the fluorimetric determination of copper in toluene. The excitation and emission wavelengths were 370 nm and 440 nm respectively. A linear calibration curve was obtained with 0-2 $\mu\text{g/ml}$ copper in toluene. The copper in copper wires were determined and were found 79.6% (C.V. 2.5%) as compared to 82% (C.V. 0.8%) using atomic absorption

Introduction

A number of complexing reagents have been used for the fluorimetric determination of copper(II), nickel(II), palladium(II), cobalt(II) and oxovanadium(IV) [1-2]. The analysis of copper (II) by fluorescence have been reviewed, based on (i) fluorescence quenching, (ii) reduction of copper (II), (iii) formation of ternary complex, (iv) use of polycrystalline containing ion activators, (v) chemiluminescence, (vi) the catalytic effects of copper(II), (vii) use of enzymes, (viii) reagent oxidation and (ix) chelate formation [3]. Recently a number of methods have been reported for copper determination based on catalytic fluorimetric methods [4-7], fluorescence quenching methods [8-10] and chelate formation [11,12].

The tetradentate ligand bis(salicylaldehyde) tetramethylethylenediimine (H_2SA_2Ten) reacts with copper(II), nickel(II), palladium(II), cobalt(II) and oxovanadium(IV) to form coloured complexes, but the complexes are not sensitive for spectrophotometric determination of metal ions [13]. It is therefore in the present work we have examined the reagent for fluorimetric determination of metal ions. A spectrofluorimetric

method has been developed for the determination of copper in copper wires.

Results and Discussion

The copper(II), nickel(II), palladium(II) and oxovanadium(IV) complexes were prepared as reported earlier [13]. The results of elemental micro analysis for cobalt(II) chelate prepared in the present work agreed reasonably to the expected values. IR spectral bands also agreed reasonably as expected from its structure. The solution of the reagent and its copper(II), nickel(II), cobalt(II), palladium(II) and oxovanadium(IV) complexes in chloroform were examined on spectrofluorimeter. Different excitation wavelengths were fixed, after recording their absorption spectra on spectrophotometer. Emission wavelength was varied to obtain stable response for each of the species.

Table 1 indicates the excitation and emission wavelengths for the optimal response for the reagent and its metal chelates. The change in emission intensity with the concentration of metal chelates was recorded and linear calibration curves

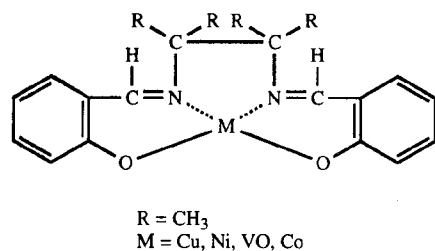


Fig. 1: Structural diagrams of reagent and its metal chelates.

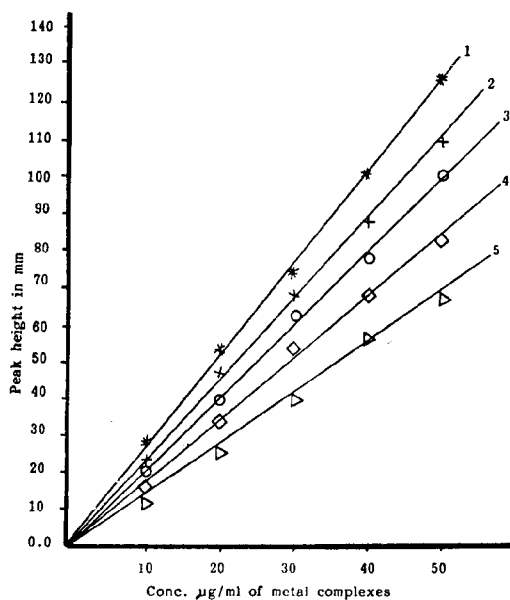


Fig. 2: Calibration curves of metal chelates (1) cobalt (2) palladium (3) oxovanadium (4) copper (5) nickel in chloroform. Excitation and emission wavelengths as Table 1.

were obtained with 0-50 µg/ml of each of the complex (Fig. 2). Cobalt(II) complex indicates maximum sensitivity, followed by in sequence palladium(II), oxovanadium(IV), copper(II) and nickel(II) complex using same instrumental sensitivity.

Table 1: Optimal excitation and emission wavelengths for fluorescence measurement of reagent and their metal chelates

Compound	Excitation wavelengths nm	Emission wavelength nm
H ₂ SA ₂ Ten	360	440
SA ₂ TenPd	330	370
SA ₂ TenCo	340	400
SA ₂ TenVO	365	430
SA ₂ TenCu	370	440
SA ₂ TenNi	340	420

In order to use the reagent H₂SA₂Ten for fluorimetric determination of copper, solvent extraction procedure was used. The problem was encountered because of the emission of the reagent at the wavelength of copper. Different organic solvents and buffers were tried to extract selectively copper(II) complex and strip off the remaining reagent from organic phase. Toluene proved a better solvent for the extraction of copper complex and sodium bicarbonate (0.5 mol) pH=8 proved satisfactory for the retention of the reagent in aqueous phase. However the washing of the organic layer with buffer solution removed completely the reagent from the organic phase to aqueous phase. A linear calibration curve was obtained at a final concentration of 0-2 µg/ml of copper in toluene (Fig. 3). The test solutions of copper were analysed and relative % error was found within 0-6.25%. The copper contents in copper wire was determined and was found 79.6% with coefficient of variation 2.5% (n=3). The results obtained were compared using atomic absorption and was found 82.0% with coefficient of variation 0.8%. The results agree reasonably with each other and no significant difference is indicated at 95% confidence level.

Effect of diverse ion on the extraction and determination of copper was investigated, cations sodium(I), potassium(I), calcium(II), magnesium(II), barium(II), manganese(II) aluminium (III),

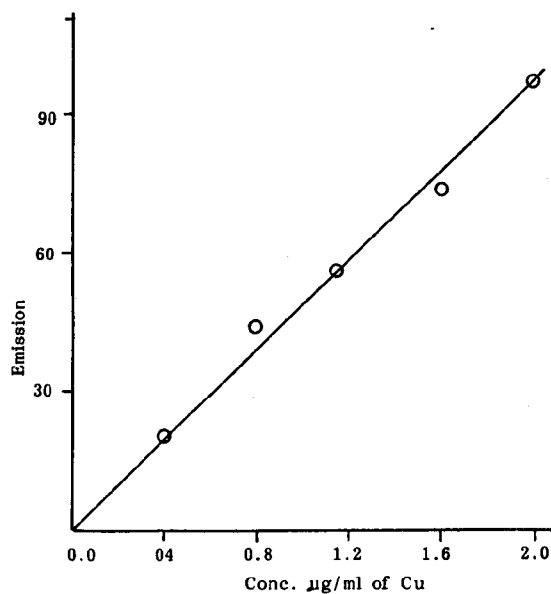


Fig. 3: Calibration curve for the extraction of copper in toluene.

uranium(VI), mercury(II), lead(II) molybdenum (VI) and anions citrate tetrates, oxalate, phosphate, chlorate and fluoride when present ten times the concentration of copper did not interfere. In case of aluminium, sodium fluoride (1 ml, 1%) was added. However the metal ions copper(II), nickel(II), oxovanadium(IV) and palladium(II) are simultaneously extracted with copper(II) and interfere the copper(II) determination and may be separated before determination.

Experimental

The reagent H_2SA_2Ten and its copper(II), nickel(II), palladium(II) and oxovanadium(IV) complexes (Fig. 1) were prepared as reported [13,14]. The cobalt(II) complexes were prepared as under:

Pure nitrogen gas was passed through a solution of cobalt(II) acetate (0.249 g, 0.001 mole) in water (5 ml). The reagent H_2SA_2Ten (0.324 g, 0.001 mole) dissolved in methanol (5 ml) was added to the cobalt(II) solution. The nitrogen gas was continued to pass and mixture was refluxed for 20 min. The mixture was cooled. The precipitate formed was filtered m.p. > 342°C. Calculated for $C_{20}H_{22}N_2O_2Co$, requires % C=63.00, H=5.77, N=7.35, found % C=62.80; H=5.78 and N=7.53. IR (KBr) cm^{-1} (rel. intensity) 1615 (vs), 1590(s), 1530(vs), 65(m), 535(m), 465(m), UV and VIS in $CHCl_3$, λ_{max} nm (ϵ 1. mole, cm^{-1}) 490(800), 410(7050), 340(6700), 255 (18800).

Hitachi F 1200 fluorescence spectrophotometer was used for fluorescence measurements. A weighed amount of each of pure complex was dissolved in chloroform and after necessary dilution with chloroform, was examined fluorimetrically. Elemental micro-analysis was carried out at H.E.J. Research Institute of Chemistry, University of Karachi. Spectrophotometric studies were carried out on Hitachi 220 spectrophotometer. Infra red spectrum of cobalt(II) complex in KBr was recorded on Perkin-Elmer 1430 IR spectrophotometer.

Solvent extraction of copper

To an aliquot of solution (1-4 ml) containing (0-10 μg) of copper was added 2 ml bicarbonate buffer (pH 8), reagent solution (0.5 ml, 1% w/v) in methanol and was heated on water bath (60-70°C) for 5 min. The contents were allowed to

cool and were transferred to separating funnel. Toluene (5 ml) was added and the contents were mixed well. The layers were allowed to separate. The aqueous layer was drained out. To the organic layer was added bicarbonate buffer (pH = 8) (4 ml). The contents were again mixed well and layers were allowed to separate. The organic layer was collected and its fluorescence was measured at 440 nm (excitation 370 nm).

Analysis of copper in wire

Copper wire (1.0174 g) was dissolved in hydrochloric acid (5 ml) and nitric acid (2 ml), and was heated to near dryness. The residue was dissolved in water and volume was adjusted to 100 ml. The solution 1.0 ml was further diluted to 100 ml and 0.1 ml of the solution was used for fluorimetric determination using solvent extraction procedure.

The copper in a copper wire was also analysed using Varian Spectr-AA-20 atomic absorption spectrometer using air-acetylene flame.

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