

Photometric determination of copper(II) by adsorption of its 1-phenyl-3-(2-thiazolyl) thiourea complex on polyurethane foam

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Adsorption of 1-phenyl-3-(2-thiazolyl) thiourea-copper(II) complex on polyurethane foam has been studied and a new method is described for the photometric determination of copper(II). The complex can be extracted into chloroform and it has λ_{\max} at 465 nm. The absorbance shows a linear relationship over the concentration range 10-100 μg Cu(II) in 10 ml chloroform. The molar absorptivity and sensitivity are found to be $1.37 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.014 \mu\text{g cm}^{-2}$ of Cu(II) for 0.001 absorbance respectively. The method has been successfully applied for the estimation of micro amounts of copper(II) in alloys.

Thiourea and its substituted derivatives have been investigated as analytical reagents in the determination of metal ions¹⁻². These compounds react with many metal ions to give colour reactions of analytical importance. The presence of three coordinating groups, two amino and one thiocarbonyl in thiourea leads to formation of polynuclear complexes³, where amino group acts as a bridging unit. Diverse spectrophotometric reagents have been reported for the photometric determination of copper(II)⁴⁻⁷. The present note describes a new method based on adsorption of newly synthesized copper(II)-1-phenyl-3-(2-thiazolyl) thiourea complex on polyurethane foam (commercial 'U' foam) and subsequent determination of copper(II) spectrophotometrically. The polyurethane foam can be re-used.

The use of polyurethane foam as an adsorbent in 'Solid-Liquid Extraction' technique as modified by Bowen⁸ offers low solubility of the extractant, easy use of large phase ratios, easy separation of phases and a synergistic extraction effect unlike that in liquid-liquid extraction. The results have been compared with the liquid-liquid extraction technique (sensitivity $0.019 \mu\text{g cm}^{-2}$). It is evident that the proposed method (sensitivity $0.014 \mu\text{g}$

cm^{-2}) is more sensitive in comparison to the liquid-liquid extraction technique for spectrophotometric determination of copper(II). Conditions have been optimised for the determination of copper(II) in various alloys.

Experimental

All chemicals used were of AR grade. A standard stock solution of copper(II) (1000 ppm) was prepared by dissolving 1 g copper foil in aqua regia and the volume made upto one litre using doubly distilled water. Standard solution of copper(II) (20 ppm) was prepared from the stock solution by dilution with distilled water. A 0.2% solution of the reagent, 1-phenyl-3-(2-thiazolyl) thiourea was prepared in ethanol. Buffer solutions of different pH values were prepared.

A GS-5701 EC spectrophotometer and Sytronics digital pH meter 335 were used for absorbance and pH measurements respectively. Polyurethane foam (commercial 'U' foam) pieces of about 1 cm^3 size were taken and prepared by the method of Hamon *et al.*⁹. The foam pieces were soaked in 1 M hydrochloric acid for about 10 h for removal of possible inorganic contaminants. The pieces were rinsed thoroughly with distilled water, squeezed and dried in air before use. The polymeric properties were found to remain intact as a result of these treatments.

An aliquot (2.0 ml) of standard copper(II) solution was taken in a flask. To it, 0.2% reagent solution (3 ml) was added. The pH was adjusted to 3.5 using acetate buffer solution. The volume was made to 10 ml with distilled water. The contents were allowed to stand for a few minutes for complete development of colour. Then four foam pieces (already prepared) were added to it. The flask was stoppered and shaken vigorously to ensure complete adsorption of the complex on the foam. The foam pieces containing the adsorbed complex were squeezed manually with a glass plunger and then transferred to another beaker where they were further squeezed out for removal of excess of reagent, if any. The complex was eluted from foam by squeezing with two portions of 5.0 ml chloroform. Traces of water were removed by adding anhydrous sodium sulphate and the absorbance measured in a 1 cm cell at 465 nm against reagent blank. Calibration curves were

constructed with different concentrations of copper(II) solutions under similar conditions.

Results and discussion

The optimum pH range for the adsorption investigations was found to be 2.0-6.5. Adsorption of copper(II) was quantitative when 2.0-5.5 ml of 0.2% 1-phenyl-3-(2-thiazolyl) thiourea and 3.0 ml buffer solution was used. Formation of complex was completed within a few minutes. Two to six prepared foam pieces were found to be sufficient for complete adsorption of the complex. The absorbance spectra of the copper(II) complex was recorded over 380-640 nm. An absorbance maximum at 465 nm was observed. The absorbance showed linear relationship in the range 10-100 μg of copper(II). The molar absorptivity was found to be $1.37 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 465 nm. The sensitivity was 0.014 $\mu\text{g cm}^2$ of copper(II) for the mean absorbance of 0.001. The sample solution containing 70 μg of copper(II) complex gave mean a absorbance of 0.512 and a relative standard deviation of 0.72%.

Tolerance of diverse metal ions on the copper(II) reagent complex was examined. The tolerance limit (in μg) is given in parenthesis. Co(II)(100), Ni(II)(100), Bi(III)(100), Ti(IV)(100), Pt(IV)(100), V(V)(100), Pb(II)(150), Fe(III)(150) and Mn(II)(200), Pd(II)(200), Cr(III)(200), U(VI)(200).

Determination of copper(II) in alloys

Synthetic solutions corresponding to the composition of some alloys of copper were prepared and analysed for their copper content. Monel wire and Brass sample No. 41.2 were taken for this purpose which have a certified composition of Ni: 66.24, Cu: 31.18, Fe: 1.18, Mn: 1.08, Mg: 0.093, Al: 0.093, Si: 0.083, C: 0.083, S: 0.0037 and Cu: 58.18, Pb: 2.56, Zn: 38.99, Fe: 0.09, Sn: 0.12 respectively. The amounts of copper taken for Monel wire and Brass No. 41.2 were 50.00 μg and 70.00 μg respectively. Five determinations were made for each alloy. The average amount of copper found for Monel wire was 49.94 μg with an error -0.12%. For Brass No. 41.2 (the average amount of copper(II) found was 70.26 μg with a percentage error of +0.37%.

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