

EXTRACTION—SPECTROPHOTOMETRIC SUB-MICRODETERMINATION OF COPPER WITH 2-FURFURYL THIOSEMICARBAZONE

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Abstract. A rapid and selective extraction-spectrophotometric method is proposed for the determination of sub-micro amounts of copper. 2-furfuryl thiosemicarbazone forms a coloured complex with copper which is quantitatively extractable in chloroform. The colour is stable at least for 4 hours. Beer's law is obeyed upto 18 μg of copper. The molar absorptivity at 370 nm is 2.86×10^4 $\text{l mole}^{-1} \text{cm}^{-1}$. Most of the common cations and anions do not interfere.

The widely advocated chelating – hypothesis postulates that the antituberculous activity of compound is associated with its ability to form stable complexes¹ with metals like copper and iron. During similar investigations with furfuryl compounds, a literature survey showed that thiosemicarbazones and substituted thiosemicarbazides have been used for the spectrophotometric determination of manganese², cobalt^{3,4}, nickel⁵, iron⁶, platinum^{7,8,9}, rhenium¹⁰, bismuth¹¹, vanadium¹², and zinc¹³. Komatsu¹⁴ used l-acetylthiosemicarbazide for the direct determination of copper, but reported the interference of several ions. Fluorescent properties of some thiosemicarbazide complex with gallium,¹⁵ have advantageously been used for analysis. Herein, the use of 2-furfural thiosemicarbazone as a reagent for the selective extraction and spectrophotometric determination of copper is described. The method is rapid, sensitive and needs no critical experimental conditions.

Experimental

Reagents. 2-furfural thiosemicarbazone (FTSC) was synthesized as follows: A mixture of freshly distilled furfural (0.5 mole) thiosemicarbazide (0.5 mole) and acetic acid (0.1 mole) in absolute alcohol was refluxed for 4 hr and the mixture concentrated under vacuum and then left overnight at room temperature. Almost colourless crystalline needles of FTSC were filtered, washed with cold ether and dried under vacuum. The product, FTSC, was crystallized from ethyl alcohol to obtain colourless needles (yield 0.4 moles). Its m.p. was 150.^o

A 0.25% w/v stock solution of FTSC in ethyl alcohol was prepared, and 0.01% FTSC solution was obtained by diluting the colourless stock solution

with alcohol. The FTSC ethyl alcohol solution turns slightly yellow after standing for two to three weeks, in which case a fresh stock solution should be prepared. Standard copper (II) solution was prepared by dissolving 2.78 g of copper (II) chloride dihydrate in 1:1 litre of deionized water. The solution was made acidic by the addition of dilute hydrochloric acid (approximately 0.02 M). The solution was standardized by titration with 0.01 M IEDTA solution. The volume of this solution was adjusted to obtain 0.5 g/litre of Cu (II) stock solution. All working solutions of copper were obtained by dilution of the stock solution.

Buffer Solutions. 0.2 M acetic acid-0.2M sodium acetate (pH 4-5.9), 0.2M dipotassium hydrogen phosphate and 0.2M sodium hydroxide (pH 6-9). These buffers were used according to the pH desired.

All reagents were of analytical grade and used without further purification.

Apparatus. Optical densities at a fixed wave-length (370 nm) were measured with a Unicam SP 600-2 spectrophotometer and the spectra of solutions were recorded with a Beckman DGBT spectrophotometer. 1.0 cm glass or quartz cells were used as appropriate. For pH measurements, a pH M4 Radiometer with Glass-Calomel electrodes was used.

Procedure

Transfer an aliquot of solution containing 2-18 μg of Cu (II) into a 50 ml separatory funnel. Add 1.0 ml of acetate buffer solution (pH 5.9). Bring the volume to about 20 ml by adding deionized water. Add 2.0 ml of (0.01% w/v) solution of FTSC. Add 10.0 ml of chloroform. Shake the mixture for 15 min and separate the chloroform layer into a 25 ml stoppered bottle containing anhydrous sodium sulphate. Record the absorbance of the solution at 370 nm with 0.01% FTSC solution as blank. The amount of the copper can

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be determined from the calibration curve.

Results and Discussion

Absorption Spectra. The copper-FTSC complex has absorption maximum at 370 nm, but the band is reasonably broad and does not need narrow wave band setting for precise absorbance measurement. Experiments for the copper-FTSC system were designed to cover a 10 fold change in copper concentration. Other parameters, such as pH and FTSC concentration, were also varied, but in no case any significant shift in absorption maximum was observed, indicating that the equilibrium system remains practically unchanged and there is a single predominant stable complex in the range of copper concentrations investigated.

Effect of pH. Keeping the copper concentration, phase ratio and FTSC concentration constant, the influence of pH on the absorbance of the extracted species was investigated. The results of this study are given in Fig.1. From Fig.1 it can be seen that the absorbance of the Cu-FTSC complex reaches maximum at pH 5.4 and above, and remains practically constant up to pH 9.2. Acetate buffer (pH 5.9) was, however, chosen as recommended in the procedure for experimental purposes.

Stoichiometry of the Extracted Species. In Fig. 2 are given the results of Yoe and Jones's¹⁶ molar ratio method for determining the formula of the complex. Ionic strength of the aqueous phase was kept at 0.1 (Fig.2). Extrapolations of the linear portions of the curve (absorbance versus the molar ratio of FTSC/Cu) intersect where the molar ratio of FTSC to copper is 2, indicating a ligand to metal ratio of 2:1. The curve further suggests that a three-fold molar excess of

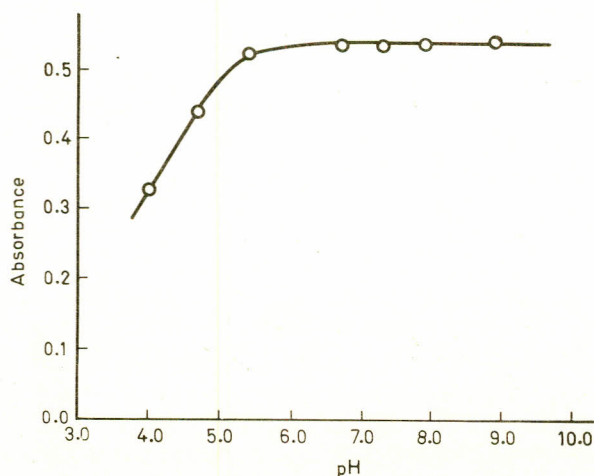


Fig. 1. Effect of pH on the absorbance of FTSC-Cu(II) complex, Cu 12 μg , FTSC 0.01%, $V_{\text{aq}}/V_{\text{org}} = 2$.

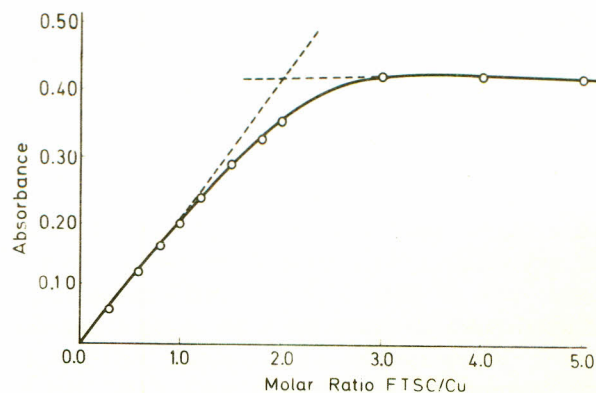


Fig. 2. Molar ratio plot at pH 5.9, total concentration of copper and FTSC, 1.3×10^{-4} M, 370 nm. Ionic strength 0.1. Dashed lines - extrapolated linear portions. Solid line passes through the experimental points. Reagent blank, 370 nm.

FTSC over copper is needed to attain a reproducible absorbance. Yoe and Jones's molar ratio method was extended to a FTSC/Cu ratio of 10 (not shown in Fig.2) and it was found that a ten fold molar excess of the reagent was tolerated by the system and the absorbance remained constant.

Effect of Shaking Time. The absorbance of the extract from 5 μg of copper in the aqueous phase was measured as a function of shaking time. The system attained equilibrium within 15 min and with increase of shaking time to 60 min, the absorbance remained constant.

Effect of Phase Volume Ratio. At pH 5.9, the same amount (5 μg) of copper present in varying volumes of the aqueous phase (V_{aq}) was extracted into 10.0 ml of chloroform (V_{org}). The extraction was quantitative and the absorbance remained unchanged upto a phase volume ratio, $V_{\text{aq}}/V_{\text{org}}$, of 5.

Beer's Law and Stability of Colour. The absorbance of the extract as a function of the concentration of copper taken, followed Beer's law upto 18 μg of copper. The optimum concentration range as evaluated by Ringbom's¹⁷ method was 0.3 ppm to 1.8 ppm. The molar absorptivity at 370 nm was calculated to be $2.86 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$. The sensitivity, as defined by Sandell¹⁸ was $0.01 \mu\text{g Cu cm}^{-2}$. The absorbance of the extracted complex remained unchanged at least for 4 hr.

Effect of Foreign Ions. The interference caused by diverse ions was studied by determining 5.0 μg of copper containing the diverse ion by the prescribed procedure and its absorbance compared with a similar aliquot of copper without the diverse ion. Keeping a tolerance limit of 0.005 in absorbance, it was found that following ions (μg in parentheses) did not

appreciably interfere. Al^{3+} (70), Ca^{2+} (108), Cd^{2+} (60), Fe^{2+} (25), Fe^{3+} (60), Ni^{2+} (5), Mn^{2+} (75), Co^{2+} (20), Cr^{3+} (20), Zn^{2+} (20), Zr^{4+} (15), Au^{3+} (5) Iodide (1000), Sulphate (1000), Chloride (1000), Phosphate (1000) and Acetate (1000). Presence of Au^{3+} (20) and Ni^{2+} (25) gave 1.6 and 2.3 per cent relative errors respectively, while Co^{2+} (100), Au^{3+} (75) and citrate (1000) seriously interfered giving a relative error of 10.0, 17.7 and 76.0% respectively. The interference of citrate ion is due to the formation of Cu^{2+} - citrate complexes which remain unextracted. Au^{3+} forms extractable complex with FTSC, but it does not interfere when present in equal amount. Interference from 15 to 20 fold excess Au^{3+} could, however, be avoided by reducing the Au^{3+} by the addition of Fe^{2+} in the aqueous phase prior to adding the reagent.

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