

1-(4'-Chlorophenyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol as an Effective Reagent for the Spectrophotometric Determination of Copper After Synergic Extraction

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The proposed method describes the synergic solvent extraction and spectrophotometric determination of copper(II) with 1-(4'-chlorophenyl)-4,4,6-trimethyl (1H, 4H)-2-pyrimidinethiol in combination with pyridine at pH 5. The extracted 1 : 2 : 2 Cu(II)-thiol-pyridine complex absorbs at 400 nm, the molar absorptivity is $1.160 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and Sandell sensitivity is 5.5 ng cm^{-2} . Beer's law is obeyed over the range 5-70 μg of copper per 10 ml of chloroform. The method has been used to determine copper in synthetic mixture, alloys, plant material and drugs.

Pyrimidinethiols, also known as cyclic thioureas, constitute a versatile class of analytical reagents. Singh *et al.* have reviewed the analytical aspects of the chemistry of substituted pyrimidinethiols¹. The use of such compounds as extractants for the platinum group metals and gold was investigated in our laboratory²⁻⁴. In the present paper we describe the synergic solvent extraction of copper(II) with 1-(4'-chlorophenyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol (4'-chloro-PTPT) in combination with pyridine from an aqueous solution of pH 5.0. The chloroform extractable complex is quite stable and hence suitable for the spectrophotometric determination of copper(II) at 400 nm.

The method proposed here is rapid, simple, sensitive and provides separation of microgram amounts of copper(II) from many associated elements.

Materials and Methods

All the chemicals used were of AR grade. A stock solution (1 mg/ml of copper) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water and a few drops of conc sulphuric acid were added. It was standardised by a standard method. Solutions of lower concentration were obtained by appropriate dilution as required.

4'-Chloro-PTPT was prepared by the method of Mathes⁵ using 4-chloroaniline and was purified by repeated crystallizations until fine colourless crystals (m.p. 188°) were obtained.

A 0.5 M pyridine solution was prepared by dissolving a weighed amount of the base in chloroform. Equal volumes (5 ml each) of the base solution and 0.01 M thiol solution in chloroform were mixed and used as the extraction solution.

A Beckman DU-2 spectrophotometer with 1-cm quartz cells was used for absorbance measurements. The pH was measured with a Phillips pH meter.

General procedure

An aliquot of the sample solution containing 5-70 μg of copper was taken and pH adjusted to 5.0 in 25 ml volume with 0.1 M hydrochloric acid and sodium hydroxide solutions. The solution was transferred into a 100 ml separatory funnel and mixed thoroughly with 10 ml extracting solution for 1 min. The two phases were allowed to separate and the absorbance of the organic phase was measured against chloroform at 400 nm. The copper content was computed from a calibration graph.

Results and Discussion

The extraction of copper was studied at various pH values. In the absence of pyridine, extraction of 30 μg of copper(II) with 0.05 mM of the reagent in chloroform commenced at pH 6 and became quantitative at pH 8.5 after shaking for 5 min. In the presence of pyridine and 0.02 mM of the reagent, however, extraction started at pH 2.5 and became quantitative at pH 4. The extraction equilibrium was attained on shaking for 15 sec only. In the present work the mixture was shaken for 1 min in order to ensure complete extraction. Pyridine thus shows a synergic effect in the extraction of copper(II)-thiol complex from an acidic medium. After extraction the pH of the aqueous phase was found to be ≈ 6.3 . The chloroform extract showed a maximum absorbance at 400 nm. The Sandell sensitivity of the colour reaction was 5.5 ng cm^{-2} with molar extinction coefficient of $1.16 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Beer's law was obeyed over the concentration range 5-7 μg of copper per 10 ml of the organic phase. The complex was stable for 12 hr.

Effect of diverse ions

In order to assess the possible analytical applications of the copper-thiol complex, the effect of a few

foreign ions that often accompany copper was studied. Various amounts of ionic species were added to the sample solution containing 30 μg of copper(II) and the above general procedure was applied. An error of $\pm 2\%$ in the absorbance readings was considered tolerable. The interference studies showed that cations, namely iron (II & III), molybdenum(VI), tin(II), tellurium(IV), titanium(IV) and bismuth(III) interfered. There was no interference from 10 mg each of lead(II), cadmium(II), uranium(VI) and vanadium(V); 5 mg each of nickel(II), cobalt(II), chromium(VI), manganese(II), magnesium(II), zinc(II), selenium(IV), cerium(IV), ruthenium(III), rhodium(III), iridium(III) and platinum(IV); 1 mg each of silver(I), thallium(I), thorium(IV) and tungsten(VI). The method could also tolerate 0.5 mg each of gallium(III), mercury(II), aluminium(III), zirconium(VI) and rhenium(VII). There was coextraction of palladium(II), osmium(VIII) and gold(III), but interferences due to these cations were removed by selective prior extraction²⁻⁴. The interference of iron(III) was eliminated by prior extraction with isobutyl methyl ketone in 6 M hydrochloric acid. But the complexing anions interfere severely and must be absent.

The Job plots shown in Figs 1 and 2 indicate formation of 2 : 1 (L : Cu or Py : Cu) as well as 1 : 1 complexes in both the cases. This explains the non-integral slope of 1.35 in the case of log D-log C (thiol) plot at constant pyridine concentration (Fig. 3) and a slope of 1.27 in the case of log D - log C (pyridine) plot at constant thiol concentration (Fig. 4). In the presence of reducing agents like iron(II), tin(II) and ascorbic acid, there is no complex formation indicating that only copper(II) reacts with the reagent. The copper(II) - thiol complex is extractable into chloroform; hence the probable composition of the uncharged complex is CuL_2Py_2 (1 : 2 : 2).

The synergic effect in the extraction is attributable to the formation of the readily extracted pyridine adduct as it is evident from the very high absorbance at 0.1 mol fraction of copper in Fig. 2 as against the low absorbance found at mol fractions of copper above 0.8 in Fig. 1.

Determination of copper in alloys

About 0.5 g each of brass, copper-nickel alloy, gun metal and nickel-silver alloy was taken and brought into solution according to the standard procedure⁶. Similarly 0.1 g of gold-copper-silver alloy was taken and its solution was prepared as described earlier⁴. Appropriate aliquot of the sample solution obtained was taken and the pH of the solution was adjusted to 5.0 in 25 ml volume with 0.1 M hydrochloric acid and sodium hydroxide solutions. Copper was determined

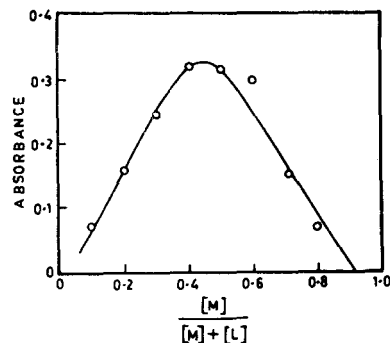


Fig. 1—Job plot at pH 5.0 {[copper]=[LH] = 4.724×10^{-4} M; [pyridine] = 0.5 M}

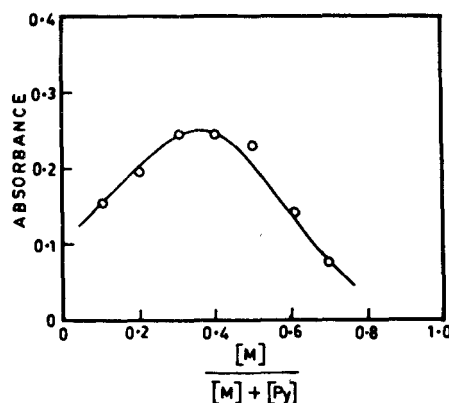


Fig. 2—Job plot at pH = 5.0 {[copper]=[pyridine] = 7.873×10^{-4} M; [LH] = 0.01 M}

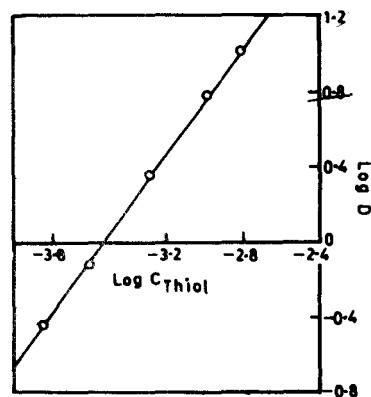


Fig. 3—Log D - Log C (thiol) plot at constant pyridine concentration; [pyridine] = 0.5 M; pH = 5.0.

by the proposed method. Results of analysis of some standard samples are reported in Table 1. The recovery of copper in alloys is in agreement with the certified values.

Determination of copper in plant material: Analysis of cane-sugar leaves of Clones Co 419 and Co 740

A six month old leaf sampling (third leaf from top) was done randomly. The sampled leaves after removing the midrib were cut into one sq cm pieces and dried in oven at 80° till constant weight was obtained.

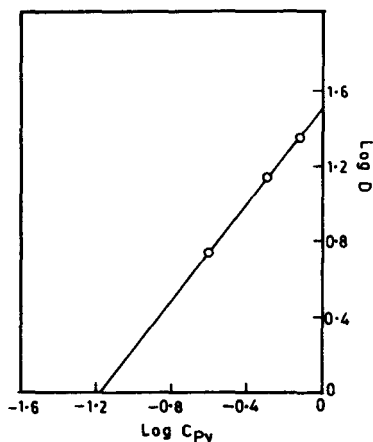


Fig. 4—Log D = log C (pyridine) plot at constant thiol concentration; [thiol] = 0.01 M; pH = 5.0.

The dried leaf material was crushed into fine powder. The powdered material (2 g) was treated with 20 ml of a mixture of nitric acid + perchloric acid + sulphuric acid in the proportion of 10 : 3 : 1 and digested on a hot plate. The solution was diluted and the precipitated silica was removed by filtration. The filtrate was evaporated to near dryness. The residue was leached with water. From this, iron was removed by extracting twice with 10 ml portions of isobutyl methyl ketone keeping the solution 6 M with respect to hydrochloric acid. The aqueous phase was slowly evaporated to dryness in order to remove excess hydrochloric acid. The residue was leached with distilled water and copper content was determined by the recommended procedure. The data obtained for different samples are presented in Table 2. The results agree well with the previously reported value⁷.

Determination of copper in drugs

The samples (1-2 tablets) were heated with the minimum amount of concentrated hydrochloric acid followed by the addition of 2-3 drops of concentrated nitric acid. The organic matter was destroyed by treatment with 5 ml of concentrated perchloric acid. The solution was slowly evaporated almost to dryness and the residue was dissolved in dilute hydrochloric acid. The solution was made 6 M with respect to hydrochloric acid and iron was extracted twice with 10 ml portions of isobutyl methyl ketone. The aqueous phase was slowly evaporated to dryness in order to remove excess hydrochloric acid. The residue was dissolved in hot dilute acid and made up to 100 ml with distilled water. Copper content was determined by the recommended procedure. The results were found to be satisfactory and are presented in Table 3.

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Table 1—Determination of Copper in Alloys

Alloy	Composition of alloy, %	Copper		Relative mean dev. (%)
		Certified value, (%)	Found* (%)	
Brass	Zn, 39.01	60.99	61.05	0.1
Copper-nickel alloy	Ni, 25.2; Mn, 0.1; Fe, 0.03	74.62	74.62	0.1
Gun metal alloy	Sn, 4.49; Sb, 0.31; Pb, 2.31.	84.95	84.52	0.5
Nickel-silver alloy	Ni, 17.0; Pb, 0.1; Sn, 0.05; Mn, 0.21.	54.60	54.60	0.1
Gold-copper-silver alloy	Au, 43.4; Ag, 7.25	49.35	49.22	0.2
Gold-copper-silver alloy	Au, 60; Ag, 5.	35.00	34.97	0.1

*Average of six determinations

Table 2—Determination of Copper in Plant Material

Clones	Copper, ppm		Relative st. dev. (%)
	AAS analysis	Present method	
Co 419	16.6	16.1-17.0	7
Co 740	18.2	17.6-18.5	4.5

Table 3—Determination of Copper in Drugs

Drug (Manufactured by)	Copper, ppm		Relative st. dev. (%)
	Taken	Found*	
Fersolate [Glaxo Laboratories (India) Ltd.]	10.36	10.28	1.4
Edinol [Bayer (India) Ltd.]	15.93	16.10	1.1
Supradyn [Roche Products Ltd., (India)]	13.51	13.50	0.2
Hem ₁₂ [Unichem Laboratories (India) Ltd.]	0.35	0.35	2.8

*Average of six determinations

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