

Cadee<sup>5</sup> distinguishes these gastropods as drillers, chippers and crushers. In the case of our described specimens, we suspect driller gastropods.

According to Keir<sup>6</sup>, many snails and parasitic worms have the capacity to excavate tunnels through the shell surface in a short time. The architecture of the tunnels in our specimens rule out the possibility of parasitic gastropods. The preferential location of the tunnels near the posterior end of the oyster shells rather indicates the action of parasitic worms. These worms possibly fed upon the waste brought out through the excurrent siphons and lived a symbiotic life with the oysters. It is further thought that the tunnels were possibly used by the worms as their protective domiciles. Finally it could be argued that the prey (oysters), the predators (gastropods) and the parasitic animals (worms) coexisted in the shallow marine habitat during the Middle Eocene when the limestones in Lakhpat were being deposited.

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# ORTHOHYDROXYACETOPHENONE THIOSEMICARBAZONE AS A NEW ANALYTICAL REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER

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THIOSEMICARBAZONES have been frequently employed as chromogenic reagents for the spectrophotometric determination of inorganic ions and their analytical potentialities have been reviewed<sup>1,2</sup>. Here we describe the synthesis of *o*-hydroxyacetophenone

thiosemicarbazone (OHAPTS) and its use as analytical reagent for the determination of copper. Most of the spectrophotometric methods reported in the literature suffer from many disadvantages—low sensitivity, heating, extraction, and tolerance limit of associated ions<sup>3-7</sup>. The proposed method, besides being sensitive, is simple and rapid, requires no heating or extraction, and has the advantage of virtual freedom from interference of many associated foreign ions. The high tolerance limit of zinc in presence of citrate allows the method to be used for the determination of copper in zinc-based alloys and steel samples.

The reagent was prepared by a procedure similar to that of Aydin<sup>8</sup> and Reddy<sup>9</sup> (yield 65%, m.p. 183–186°C). The reagent (0.5232 g) was dissolved in 50 ml of DMF ( $5 \times 10^{-2}$  M). Solutions of lower concentration were obtained by dilution with DMF. Stock solution of Cu(II) was prepared by dissolving 2.4969 g of copper sulphate pentahydrate (BDH, AR) and standardized titrimetrically<sup>10</sup>. All chemicals used were of BDH AR grade.

To each of a set of 25 ml volumetric flasks containing 12.5 ml of buffer (acetic acid–sodium acetate) of pH 5.5, 3 ml of DMF, 2 ml of reagent ( $5 \times 10^{-2}$  M) and an aliquot of copper(II) solution ( $5 \times 10^{-4}$  M) were added and made up with distilled water. The absorbance at 360 nm of each solution was measured against reagent blank. A calibration graph was drawn for the relationship between the amount of copper(II) and the absorbance.

The optimum pH range for maximum colour development was 5.5–8.0. Hence sodium acetate–acetic acid buffer of pH 5.5 was selected for further studies. A five-fold excess of the reagent is sufficient for getting maximum and constant absorbance. The order of addition of constituents (buffer, DMF, metal, reagent) has no effect on the absorbance.

A linear graph is obtained for absorbance vs amount of metal ion in the range 0.42 to 6.6  $\mu\text{g ml}^{-1}$  of copper(II). The molar absorptivity and Sandell's sensitivity of the method are  $9.5 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.00669 \mu\text{g cm}^{-2}$  respectively. The standard deviation for 10 determinations of 64  $\mu\text{g}$  of copper(II) was  $\pm 0.0006$ . The practical range of determination of copper(II) as envisaged by Ringbom's plot was 0.67 to 3.94  $\mu\text{g ml}^{-1}$ .

Vosburgh and Cooper's<sup>11</sup> method indicates the presence of one complex species in solution. Also Job's and molar ratio and slope ratio methods show the presence of 2:3 (M:L) species. The stability constant of the complex is  $6.60 \times 10^{12}$ .

Several foreign ions were examined for their effect on copper(II) in the recommended procedure for the spectrophotometric determination of copper. An error of  $\pm 2\%$  in absorbance was considered to be tolerable. The tolerance limit (in  $\mu\text{g}$ ) for various ions in the determination of  $48 \mu\text{g}$  of Cu(II) at pH 5.5 is as follows:

Pb(II), 3100; W(VI), 2760; Al(III), 1620; Mo(VI),

1440; Zr(IV), 1370; Th(IV), 1160; Cd(II), 565; Mn(II), 560; Ti(II), 480; Mg(II), 390; Ce(IV), 280; Au(III), 110; V(IV), 100; Co(II), 58; citrate, 40,000; tartrate, 34,800; iodide, 19,350; nitrate, 18,600; thiocyanate, 17,400; sulphate, 14,400; bromide, 11,950; chloride, 10,635; phosphate, 9797; fluoride 5700; oxalate, 4400. However, Ni(II), Zn(II) and Cr(III) above 300, 1500 and  $300 \mu\text{g}$  respectively interfere and can be masked

Table 1 Determination of copper in alloy steels

Steel sample	Copper ( $\mu\text{g}$ )		
	Taken	Found	Error (%)
BCS 409	17.25	17.10	0.87
	23.00	22.70	1.30
	28.75	28.60	0.52
BCS 406-I	21.00	20.90	0.48
	28.00	27.90	0.35
	35.00	34.50	1.43
BCS 406	24.00	23.60	1.67
	32.00	31.60	1.25
	40.00	39.70	0.75
SRM 94-C	50.50	49.52	1.98
	75.75	75.50	0.35
	101.00	100.75	0.25

Content (%)

	Mn	Cr	Mo	Ni	Cu	V	Co	Al	Mg	Fe	Pb	Cd
BCS 409	0.48	1.22	0.77	3.14	0.23	0.280	—	—	—	—	—	—
BCS 406-I	0.61	2.10	1.00	1.52	0.28	0.017	0.006	—	—	—	—	—
BCS 406	0.53	2.12	1.03	1.69	0.32	0.084	0.047	—	—	—	—	—
SRM 94-C	0.014	—	—	0.006	1.01	—	—	4.07	0.042	—	0.06	—
										0.0018		0.002

Table 2 Comparison of OHAPTS with other thiosemicarbazone reagents

Reagent	Molar absorptivity ( $\text{l mol}^{-1} \text{cm}^{-1}$ )
Bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone)	9200
2,2'-Dihydroxybenzophenone thiosemicarbazone	8600
3-Hydroxypicolinaldehyde thiosemicarbazone	8500
Acetophenone thiosemicarbazone	8300
Glyoxal dithiosemicarbazone	6700
p-Anisaldehyde thiosemicarbazone	6100
Acenaphthoquinone thiosemicarbazone	5800
1,2-Cyclohexanedione bithiosemicarbazone	5700
1,3-Cyclohexanedione bithiosemicarbazone monohydrochloride	5000
2-Hydroxyiminocyclohexanone thiosemicarbazone	5530
Salicylaldehyde thiosemicarbazone	4800
1,4-Cyclohexanedione bithiosemicarbazone	4100
Cyclohexane thiosemicarbazone	1300
Orthohydroxyacetophenone thiosemicarbazone	9500 (present work)



with citrate up to 1000, 20,000 and 1000  $\mu\text{g}$  respectively. Fe(III) (6100  $\mu\text{g}$ ) can be eliminated by the addition of phosphate. Ag(I) and Sn(II) interfere seriously.

In order to confirm the usefulness of the proposed spectrophotometric method, it was applied to the determination of copper in zinc-based steel samples of BCS 406, BCS 406-1, BCS 409 and SMR 94-C type (nickel, chromium and zinc masked with citrate). The results are summarized in table 1.

The reagent OHAPTS was compared with some well-known thiosemicarbazones<sup>2,12</sup> (table 2). It was found that OHAPTS is a sensitive reagent.

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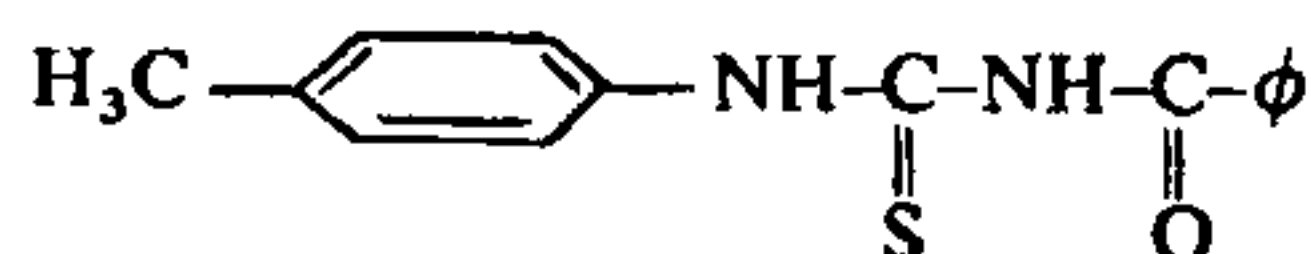
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## SYNTHESIS AND STRUCTURAL STUDIES ON THE COMPLEX OF COPPER(II) WITH *N*-(*p*-TOLYL)-*N'*-BENZOYL THIOCARBAMIDE

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*N*-(*p*-Tolyl)-*N'*-benzoyl thiocarbamide (TBTC) is a good coordinating agent<sup>1</sup>. The present communication reports interaction of copper(II) with TBTC. TBTC has been given the following structure



All the chemicals used were of BDH or equivalent grade. The ligand (TBTC) was prepared as reported in the literature<sup>2</sup>. Conductance measurements were carried out on a  $10^{-3}$  M solution of the complex. The complex was analysed for metal content using standard procedures<sup>3</sup>. Sulphur was determined as  $\text{BaSO}_4$  and carbon, hydrogen and nitrogen micro-analytically. Magnetic susceptibility measurement was made at room temperature on a Cahn-Faraday electrobalance using  $\text{Hg}[\text{CO}(\text{NCS})_4]$  as a calibrant; experimental magnetic susceptibility was corrected for diamagnetism<sup>4</sup>. The IR spectra of the ligand and the complex were recorded on a Perkin-Elmer IR spectrometer Model-621 in nujol ( $4000-200\text{ cm}^{-1}$ ). The electronic spectra of the complex were recorded on a Carry-14 spectrophotometer in nujol mull. The polycrystalline ESR spectrum of the complex at room temperature was recorded on an E-line X-band spectrometer using TCNE as *g* marker. Antifungal activity of the complex and the ligand was determined at different concentrations as described by Schmitz<sup>5</sup>.

The complex was prepared by slowly adding an aqueous ethanolic solution of cupric acetate in the presence of 1-2 drops of glacial acetic acid to a solution of TBTC in acetone in 1:2 molar ratio with constant stirring. A yellow precipitate was formed immediately. It was filtered, washed several times with water, ethanol, acetone and finally with ether, and dried *in vacuo*.

Copper(II)-TBTC complex (m.p.  $>300^\circ\text{C}$ ) is yellow and is insoluble in water, acetone, ethanol and methanol but soluble in DMF. The molar conductance of the complex in DMF is  $26\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$ , showing that it is a non-electrolyte<sup>6</sup>. Analytical data: Calculated for  $\text{Cu}(\text{TBTC})_2(\text{CH}_3-$