

## SPECTROPHOTOMETRIC DETERMINATION OF COPPER AFTER EXTRACTION OF THE Cu(II) SYSTEM BY HIGH - MOLECULAR WEIGHT AMINES

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An investigation of the complex formed between copper and thiocyanate in the presence of weak sulphuric acid solution has been carried out and its extractability by a high-molecular weight amine (HMWA) in organic solvent examined. The yellow to orange coloured Cu(II) CNS complex is quantitatively extractable from an aqueous phase into an organic phase containing Allamine 336 or tribenzylamine. On the basis of this extractability a method has been developed for the spectrophotometric determination of copper in the presence of many other interfering radicals. The extractability of the complex by HMWA suggests that the coloured species is anionic.

### INTRODUCTION

The use alkali thiocyanates as complexing agent for the colorimetric determination of a number of metals has been recognised for some time. Bock [1] made an extensive study of the extractability of many metal thiocyanate into an immiscible organic solvent. The present authors studied earlier the thiocyanate of cobalt (II) by precipitation with tetraphenyl arsonium chloride in organic solvents [2, 3]. The thiocyanate complexes of Mo [4] (IV), Ti [5] (II) and Fe [6] (III) were extracted by high molecular-weight amines and the extracted species were used for subsequent spectrophotometric determination.

Thiocyanate of copper also gives red-brown colour with copper, which was precipitated by triphenylmethylarsonium chloride (TPA) as TPA tetra-thiocyanate cuprate (II), and extracted with dichlorobenzene by Ellis and Gibson for the subsequent spectrophotometric determination of copper [7]. No attempt appears to have been made in extracting the coloured complex directly into HMWA. As the coloured species appears to be in an anionic form, investigation were made with the aim of using HMWA (which acts as liquid-anion-exchanger) to extract the species and if possible use it for the spectrophotometric determination of copper.

### EXPERIMENTAL

#### *Apparatus*

Erma. LS-7. Spectrophotometer made in Tokyo, Japan.

#### *Reagents*

1. *Copper standard solution:* 0.10 g copper metal

foil was dissolved in 1:1 nitric acid and 1 ml of concentrated sulphuric acid was added to volatilise the acids, but not to complete dryness. The residue was redissolved in distilled water, and transferred quantitatively to a one litre volumetric flask.

2. *Potassium thiocyanate:* 0.5 M aqueous solution.

3. *Sulphuric acid:* 0.10 M

4. *Acetone:* 99.9 % pure.

5. *Allamine 336:* 5 % solution in benzene.

All reagents are Analar grade.

*Formation of Cu(II) CNS complex and extraction by amines.* The yellow to orange brown complex was formed by adding thiocyanate into a solution containing copper in the presence of weak sulphuric acid. Amine solution (5 ml) in organic phase was added to the coloured solution of copper in a separating funnel and was shaken for 1-2 min. The phases were allowed to separate and the coloured complex was quantitatively extracted into the organic phases as no trace was ever found in the aqueous phase. The colour of the complex after extraction was the same as in the aqueous phase. The organic phase was collected in a dried flask after passing it through a small filter paper (5 cm) to remove suspended water droplets. The absorption spectrum was determined with respect to a blank containing all the reagents, but no copper, and extracted in the same way. The absorption spectrum shows maximum absorption at 410 m $\mu$  (Fig 1).

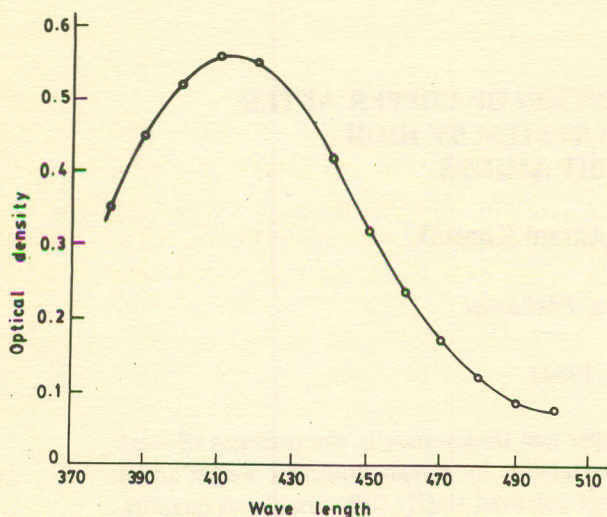


Fig. 1. Absorption spectrum of  $\text{Cu}-(\text{CNS})_2^{y-x}$  after extraction into amino phase.

#### Calibration, Sensitivity and Stability

Known concentrations of copper were extracted by the foregoing procedure and absorbance measured at 410  $\text{m}\mu$ . For solution containing between 25-250  $\mu\text{g}$  5 ml, i.e. 5 to 50 ppm. Beer's law was closely obeyed. The molar absorption coefficient is  $1 \times 10^{-3}$ . The colour of the complex is fairly stable for one hour. At the end of this period there is a gradual fading and lowering of the intensity of colour.

**Stability.** The stability of smine/organic solvent extract was found to be dependent on three factors: (i) KCNS concentration (Fig. 2); (ii) acid concentration (Fig. 3); (iii) type of solvent: and (iv) effect of temperature.

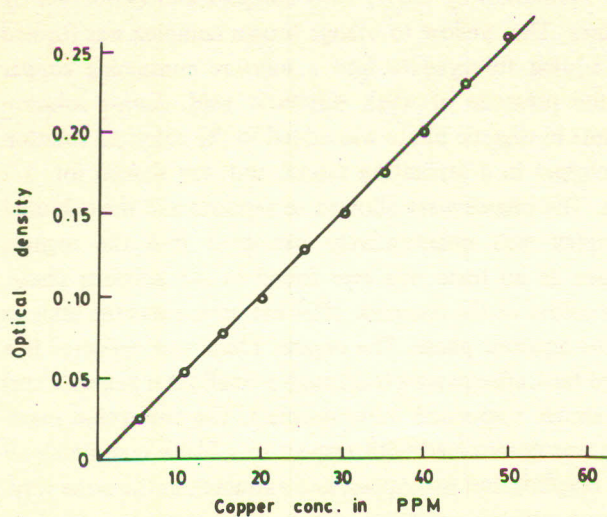


Fig. 2. Calibration curve.

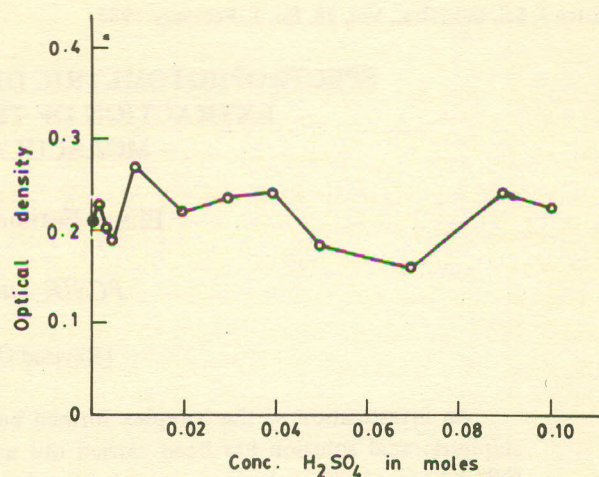


Fig. 3. Effect of  $\text{H}_2\text{SO}_4$  concentration on extraction.

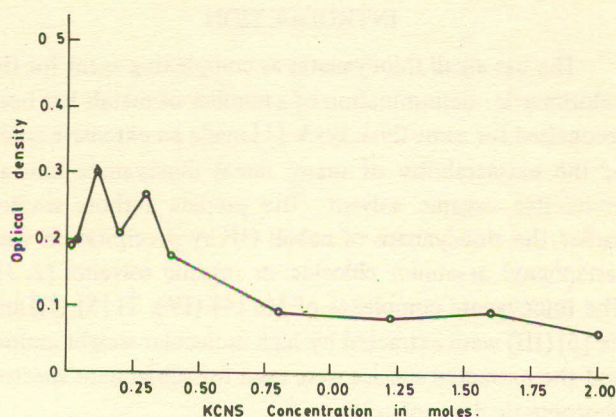


Fig. 4. Effect of KCNS concentration on extraction.

Optimum conditions found are: 0.125 molar potassium thiocyanate; 0.01 to 0.04 molar acid, pretreated amine was not found to be better than untreated amine solution. Chloroform solution of amine was not preferred because of its greater volatility and miscibility than that of the benzene solution. Moreover, when chloroform is used as the solvent, the extract is stable only for 10-15 min. after extraction and slight turbidity then appears along with fading of the colour and the results are not reproducible.

**Solvent Effect.** When chloroform is used as the solvent, the extract is stable only for a short period of 10-15 min. after extraction and slight turbidity then appears, along with fading of the colour and results are not reproducible. Pretreatment of the chloroform amine-phase with 0.1 molar sulphuric acid however gave better results in subsequent extraction of the system, when benzene solution of Allamine

336 was used as extractant. A very clear solution was obtained. This was in conformity with our earlier work in the extraction of metal anionic complex species.

*Procedure.* 2.5 ml copper solution containing 5-50  $\mu\text{g}$  copper in a separatory funnel was taken. One ml sulphuric acid (0.1 M) and 2.5 ml. potassium thiocyanate or ammonium thiocyanate and 1 ml. of pure acetone were added. (0.5 M), followed by dilution upto 10 ml. The contents were 5 ml. of amino (Allamine 336) was added. The solution in benzene was mixed with the two phases for one to two min. either manually or by the aid of mechanical machine and the phases were allowed to separate. The amine layer was filtered through a small filter paper into a 5-10 ml volumetric flask to remove the suspended water droplets. The absorbance at 410 m $\mu$  after 45 min. of extraction against a blank containing all other reagents except copper was measured.

*Constancy.* A factor requiring attention in most thiocyanate methods is the instability of the coloured solutions. A change in colour intensity may result from the reducing properties of thiocyanate or its decomposition products (causing fading of copper thiocyanate colour) or more often from the slow decomposition of thiocyanate in acidic medium. This decomposition is usually described as the polymerisation of thiocyanic acid and results in the formation of yellow product, especially in fairly strong

acidic solutions. This is one reason for extracting metal thiocyanate complexes with immiscible organic solvents [9]. Acids and other reagents like organic solvents are usually used for the purpose. Acetone is frequently added to aqueous solutions to improve colour constancy.

Various concentrations of thiocyanate and acetone in aqueous media were used. The intensity of the colour is increased twofold and the results were also found reproducible. Use of 0.5 to 1.0 ml pure acetone, however, controls the constancy of the extracted species in the presence of interfering substances.

*Interferences.* In the determination of trace metals by the above procedure, with thiocyanate three types of interferences are most frequently encountered. These are:

(i) Metal ions which form an anionic complex with  $\text{CNS}^-$  will be extracted into the amine phase, e.g.  $\text{Fe}^{+3}$ ,  $\text{Co}^{+2}$ , and  $\text{Nb}^{+3}$ , (ii) Ions which form coloured nonionic compounds with  $\text{CNS}^-$  and which are/extracted into neutral solvents, because of its solubility in these solvents e.g.  $\text{Cr}^{+3}$

(iii) Ions which oxidise  $\text{CNS}^-$  to a coloured soluble complex of indefinite composition.

With the exception of the first type fortunately none of the remaining two types interfere in the determination of copper by the foregoing procedure. As will be seen from Table 1, the first type also did not interfere seriously in the

Table 1. Effect of diverse ions

No.	Diverse ions	Conc. found	Cons. present	Error
1.	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ Containing 200 $\mu\text{g}$ $\text{PO}_4$	40 $\mu\text{g}$	40 $\mu\text{g}$	$\pm 0.00$
	" " 250 " $\text{PO}_4$	37 "	40 "	-3.00
2..	$\text{MgCl}_2$ " 200 " $\text{Mg}$	40 "	40 "	$\pm 0.00$
3.	$\text{NH}_4\text{Mg}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ " 400 " $\text{MO}$	37 "	40 "	-3.00
4.	$\text{NaF}$ " 800 " $\text{NaF}$	37 "	40 "	-3.00
5.	$\text{Na}_2\text{S}_2\text{O}_3$ " 500 " $\text{S}_2\text{O}_3$	Completely masks copper		
6.	$\text{NaH}_2\text{PO}_4 + \text{NiSO}_4$ " 100 " $\text{Ni}$ (200 $\mu\text{g}$ )	37 $\mu\text{g}$	40 $\mu\text{g}$	-3.00
7.	" + $\text{NaBiO}_3$ " 100 " $\text{Bi}$	40 "	40 "	$\pm 0.00$
8.	" + $\text{HgSO}_4$ " 100 " $\text{Hg}$	38 "	40 "	-2.00
9.	" + $\text{CdCO}_3$ " 200 " $\text{Cd}$	38 "	40 "	-2.00
10.	" + $\text{Fe}(\text{NO}_3)_3$ " 100 " $\text{Fe}$	40 "	40 "	$\pm 0.00$
11.	$\text{NaH}_2(\text{PO}_4) + \text{COCl}_2$ " 150 " $\text{CO}$ (500 $\mu\text{g}$ )	44 "	40 "	+4.00
12.	$\text{NaH}_2(\text{PO}_4) + \text{Cr}_3\text{Cl}_3$ " 100 " $\text{Cr}$ (1000 $\mu\text{g}$ )	40 "	40 "	$\pm 0.00$
13.	" $\text{BaCl}_2$ " 1000 " $\text{Ba}$	38 "	40 "	-2.00
14.	" + $\text{MnCl}_2$ " 600 " $\text{Mn}$	40 "	40 "	$\pm 0.00$

determination of copper provided these ions are present in moderate amounts. For example,  $\text{Co}^{+2}$  which forms an extractable anionic green complex gave the absorption maxima at  $620 \text{ m}\mu$  and thus did not interfere when masked properly with sodium dihydrogen phosphate. Similarly  $\text{Fe}^{+3}$  which forms a blood-red complex does not interfere even in the presence of twofold excess if used with a suitable masking agent. Sodium pyrophosphate as reported previously [10] can also be used as a masking agent. Phosphate upto  $200 \mu\text{g}$  shows no interference but at  $250 \mu\text{g}$   $40 \mu\text{g}$  copper gives a difference of  $-3 \mu\text{g}$ . Magnesium upto  $200 \mu\text{g}$  shows no interference.

Molybdenum upto  $400 \mu\text{g}$  gives a reduction of  $3 \mu\text{g}$  fluoride upto  $800 \mu\text{g}$  gives a reduction of  $3 \mu\text{g}$  & also nickel upto  $100 \mu\text{g}$  gives a reduction of  $3 \mu\text{g}$  in a solution containing  $400 \mu\text{g}$  copper.

Bismuth upto  $100 \mu\text{g}$  shows no interference. Mercury upto  $100 \mu\text{g}$  gives a reduction of  $2 \mu\text{g}$ , Cadmium upto  $200 \mu\text{g}$  gives a reduction of  $2 \mu\text{g}$ . Iron upto  $100 \mu\text{g}$  shows no interference. Cobalt upto  $150 \mu\text{g}$  gives an increase of  $4 \mu\text{g}$ . Chromium upto  $100 \mu\text{g}$  shows no interference. Barium upto  $100 \mu\text{g}$  gives a reduction of  $2 \mu\text{g}$ . Manganese up to  $600 \mu\text{g}$  shows no interference when sodium hydrogen phosphate is used as a masking agent.

From the above studies, it is evident that most of the ions associated with copper do not interfere under the above conditions, except for  $\text{Fe}^{+++}$  and  $\text{Co}^{++}$  which have been masked with a masking agent.

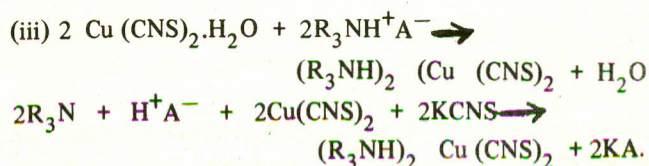
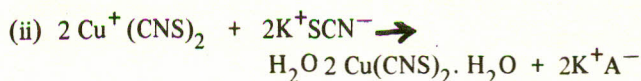
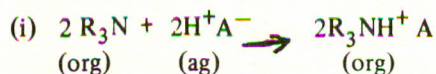
As a final check on the applicability of the system a number of unknown samples with and without interfering radicals were tested. Results are given in Table 2. Samples No. 1, 2, 3 and 4 contained copper only. Sample No. 5 contained bismuth, mercury and manganese. Sample No. 6 has nickel, sodium fluoride and lead as interfering radicals.

Table 2. Application of the method to some unknowns

Samples	Copper found	Copper present	Error
No. -1	20 ppm	20 ppm	$\pm 0.00$
No. -2	15 ppm	15 ppm	$\pm 0.00$
No. -3	10 ppm	10 ppm	$\pm 0.00$
No. -4	32 ppm	35 ppm	$\pm 3.00$
No. -5	25 ppm	25 ppm	$\pm 0.00$
Tape-water	0.00	0.00	$\pm 0.00$

## DISCUSSIONS

As indicated above, the orange yellow complex formed between  $\text{Cu(II)}$  and  $\text{CNS}^-$  in the presence of  $\text{H}_2\text{SO}_4$  (dilute) is readily extracted into Allamine 336. The instantaneous extraction of the coloured complex is indicative of the anionic nature of the complex like other metal thiocyanate complexes and liquid anion exchange occurred between the charged complex and the high molecular weight amines. The overall reaction for this type might be represented as follows:



The conclusion that the complex is anionic in nature needs to be further investigated and its structure to be established. The fact that the absorption spectra of the complex species are more or less the same with all other amines in organic phase would indicate that the absorbing species is the same in each case. The fading of colour of the complex in aqueous phase indicates the instability of the complex which when bonded with a high molecular weight amine is sufficiently stable to make use of it as a spectrophotometric method [11].

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