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Determination of Copper in Natural Waters & Sediments by Extraction Spectrophotometric Method

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A sensitive extraction spectrophotometric method has been developed based on the formation and extraction of Cu (II) - neocuproine - rosebengal into chloroform. The molar extinction coefficient of the system is 55,500 and Beer's law is obeyed up to 15 μg . Selective separation and preconcentration of Cu have been achieved through the specific reaction of Cu (I) - neocuproine and its subsequent extraction into chloroform. This has been made the basis for the determination of Cu in natural waters and sediments.

Several analytical methods have been earlier reported for the determination of Cu in natural waters. The spectrophotometric methods involving the use of biscyclohexanone oxalyldihydrazone¹ and oxalyldihydrazide² require prior concentration by ion exchange method. The sodium diethyldithiocarbamate³ method suffers from lack of sensitivity and selectivity. This has led to the adoption of neocuproine⁴⁻⁷ or 2,2 biquinoly⁸ methods because of their specificity with Cu. However, these methods lack sensitivity. A sensitive extraction spectrophotometric method has been developed based on the extraction of Cu (II) in the presence of neocuproine and rosebengal in to chloroform. This reaction is rendered selective for Cu by prior extraction of Cu (I) - neocuproine into chloroform from an aqueous solution containing EDTA and then equilibrating the organic phase with an aqueous solution containing rosebengal. The results of the new method are presented in this paper.

Absorbance measurements were made with C.Z. Spekol spectrophotometer using 5 cm corex cells. Elico model LI-120 pH meter with a combined calomel-glass electrode was used for pH adjustments.

Reagents—Copper sulphate: A stock solution of 0.01 M copper sulphate is prepared by dissolving 2.4968 g of the substance in 1 l of freshly distilled water and slightly acidifying with sulfuric acid. The working solution is prepared by diluting 10 ml of the stock solution to 1 l, (1 ml = 6 μg).

Neocuproine: A 0.1% solution is prepared by dissolving 100 mg of the substance in 100 ml of freshly distilled water.

Rosebengal: A 0.1% solution is prepared by dissolving 100 mg of the substance in 100 ml of freshly distilled water.

Hydroxylaminehydrochloride: A 10% solution is prepared in freshly distilled water.

EDTA: A 0.01 M solution of sodium salt of EDTA is prepared by dissolving 0.3722 g of the substance in 100 ml of distilled water.

Buffer: A buffer solution of pH 6 is prepared by mixing 480 ml of sodium acetate (0.2 M) and 20 ml of acetic acid (0.2 M).

All other chemicals used were of AnalaR Grade and the solvents used were freshly distilled.

Recommended procedure—(a) Dissolved free Cu in seawater: To an aliquot (100-200 ml) of filtered seawater in a separatory funnel, 2.5 ml of 10% hydroxylaminehydrochloride, 1 ml of 0.1% neocuproine were added and mixed. To this 0.5 ml of 0.01 M EDTA was added and pH adjusted to 4-6. Cu (I) - neocuproine complex was extracted into 15 ml chloroform. Quantitatively the organic phase was transferred into a separatory funnel and equilibrated for 1 min after adding 14 ml of sodium acetate-acetic acid buffer and 1 ml of 0.1% rosebengal. Organic phase was separated after 10 min into a dry test tube and the absorbance measured at 570 nm against reagent blank. The amount of Cu present in the sample can be determined from the calibration graph constructed by the same procedure.

b) Dissolved total Cu in seawater: To an aliquot (100 ml) of filtered seawater taken in a beaker, 1 ml of concentrated H₂SO₄ and 5 ml of nitric acid were added. Few boiling chips were added and cautiously evaporated to dense white SO₃ fumes on a hot plate. The heating was continued until the solution became colourless. The beaker was cooled and the solution made up to 100 ml with deionised water. The solution was neutralised and used for the estimation of Cu as in (a).

c) Cu in sediment samples: Dried (80°C) sediment (0.5 g) was made in to fine powder and digested with nitric and sulphuric acids⁹. After the completion of the

Table 1—Analysis of Seawater for Cu Using Procedure (a)
[Results average of 5 replicate determinations, and SD is 0.11]

Vol. of seawater ml	Copper present μg		
	Added	Found	Recovered
100	—	1.05	—
200	—	2.20	—
300	—	3.25	—
400	—	4.50	—
200	0.6	2.75	0.55
200	1.2	3.40	1.20
200	1.8	4.05	1.85
200	2.4	4.65	2.45

Table 2—Analysis of Cu in Different Samples

Sample	Dissolved copper $\mu\text{g/l}$	Total dissolved copper $\mu\text{g/l}$
Polluted water (Visakhapatnam harbour)	11.0	18.5
Seawater (off Visakhapatnam)	3.95	6.5
Estuarine water (Godavari, S ₂ O ₃ ²⁻ 12)	7.50	20.0
Sediment (Visakhapatnam harbour)	—	330*
Sediment (off Visakhapatnam)	—	90*

* $\mu\text{g/g}$

digestion, the solution was made up to 250 ml. An aliquot of this solution was taken and proceeded as in (a) for the estimation of Cu.

To check the recovery of Cu, known amounts of Cu were added to a fixed volume of seawater (200 ml) and Cu was determined as per the procedure (a). These results (Table 1) show that the present method is fairly reproducible and can be used for the estimation of Cu at trace levels. Table 2 shows the results obtained in the determination of Cu (av. of 5 determinations) in polluted water, natural water and sediment samples employing the present method.

The ternary complex formed with Cu (II) in the presence of neocuproine and rosebengal can be extracted quantitatively into chloroform in the pH range 5.5-7. The absorption spectrum (Fig. 1) shows a maximum at 570 nm. The molar extinction coefficient is 55,500 in chloroform and Beer's law is obeyed up to 15 μg . The chloroform extracts are quite stable (over 2 days) and 1 min equilibration is sufficient for maximum color development. The optimum concentration required for the complex formation is 20 times that of Cu (II) in the case of neocuproine and 10 times in the case of rosebengal. The composition of the ternary complex determined by Job's method of continuous variation indicates a ratio of 1:2:2 with respect to Cu

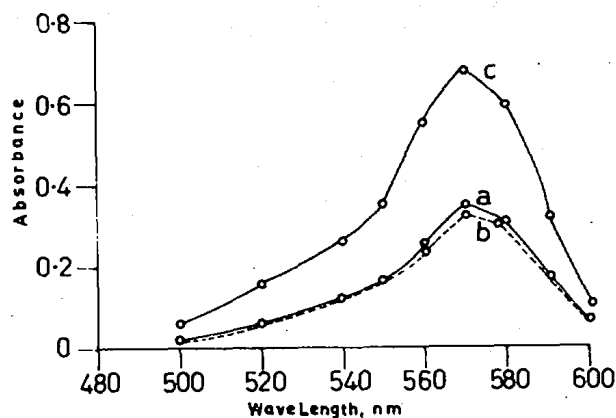


Fig. 1—Absorption spectra of Cu(II) complexes extracted into chloroform [(a) 1 ml of 10^{-4} M Cu(II) + 2 ml of 10^{-3} M neocuproine + 1 ml of 10^{-3} M rosebengal, diluted to 15 ml (pH = 6) and extracted into 15 ml of chloroform. (b) Same as (a) but as per the recommended procedure. (c) Same as (a) but with 2 ml of 10^{-4} M Cu(II).]

to neocuproine to rosebengal. Thus the species may be represented as $\text{Cu}(\text{Nc})_2^{2+} : 2\text{RB}^-$. The fact that the absorption spectrum of Cu (II)—neocuproine—rosebengal system directly extracted into chloroform is exactly the same as that of the present system as obtained from the recommended procedure reveals the final absorbing species as only Cu (II)—neocuproine—rosebengal in chloroform (Fig. 1). Evidently, the aerial oxidation of Cu (I) is taking place in the present system as suggested by Bailey *et al.*¹⁰. The estimation of Cu in high purity tellurium¹¹ has been made by the method of Bailey *et al.*¹⁰ wherein the replacement of neocuproine by orthophenanthroline in the 2nd extraction step is reported. The sensitivity of the present method ($0.018 \mu\text{g cm}^{-2}$) is comparable to that of the earlier reported method¹⁰ and at the same time, the concentration of neocuproine utilised for the separation of Cu is sufficient for the extraction of the ternary ion association complex.

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References

- 1 Nilsson G, *Acta Chem Scand*, 4 (1950) 205.
- 2 Gran G, *Anal Chim Acta*, 14 (1956) 150.
- 3 Ovenston T C J & Parker C A, *Anal Chim Acta*, 4 (1950) 135.
- 4 Gahler A R, *Anal Chem*, 26 (1954) 577.
- 5 Smith G F & McCurdy W H, *Anal Chem*, 24 (1952) 371.
- 6 Luke C L & Campbell M E, *Anal Chem*, 25 (1953) 1588.
- 7 Fulton J W & Hastings J, *Anal Chem*, 28 (1956) 174.
- 8 Tuck B & Osborn E M, *Analyst*, 85 (1960) 105.
- 9 Sandell E B, *Chemical analysis*, (Inter Science Publishing Inc New York) (1959) 278.
- 10 Bailey B W, Dagnall R M & West T S, *Talanta*, 13 (1966) 753.
- 11 Barbara K & Dobrowski J, *Chemia Analit.*, 16 (1971) 619-30 (Polish), *Analytical Abstracts*, 22 (1972) 2258.