

3500-Cu COPPER*

3500-Cu A. Introduction

1. Occurrence and Significance

Copper (Cu) is the first element in Group IB in the periodic table; it has an atomic number of 29, an atomic weight of 63.54,

and valences of 1 and 2. The average abundance of Cu in the earth's crust is 68 ppm; in soils it is 9 to 33 ppm; in streams it is 4 to 12 $\mu\text{g/L}$; and in groundwater it is <0.1 mg/L. Copper occurs in its native state, but is also found in many minerals, the most important of which are those containing sulfide compounds (e.g., chalcopyrite), but also those with oxides and carbonates. Copper is widely used in electrical wiring, roofing, various

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alloys, pigments, cooking utensils, piping, and in the chemical industry. Copper salts are used in water supply systems to control biological growths in reservoirs and distribution pipes and to catalyze the oxidation of manganese. Copper forms a number of complexes in natural waters with inorganic and organic ligands. Among the common aqueous species are Cu^{2+} , $\text{Cu}(\text{OH})_2$, and CuHCO_3^+ . Corrosion of copper-containing alloys in pipe fittings may introduce measurable amounts of copper into the water in a pipe system.

Copper is considered an essential trace element for plants and animals. Some compounds are toxic by ingestion or inhalation. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 200 $\mu\text{g}/\text{L}$. Under the lead-copper rule, the U.S. EPA drinking water 90th percentile action level is 1.3 mg/L .

3500-Cu B. Neocuproine Method

1. General Discussion

a. Principle: Cuprous ion (Cu^+) in neutral or slightly acidic solution reacts with 2,9-dimethyl-1,10-phenanthroline (neocuproine) to form a complex in which 2 moles of neocuproine are bound by 1 mole of Cu^+ ion. The complex can be extracted by a number of organic solvents, including a chloroform-methanol ($\text{CHCl}_3\text{-CH}_3\text{OH}$) mixture, to give a yellow solution with a molar absorptivity of about 8000 at 457 nm. The reaction is virtually specific for copper; the color follows Beer's law up to a concentration of 0.2 $\text{mg Cu}/25\text{ mL solvent}$; full color development is obtained when the pH of the aqueous solution is between 3 and 9; the color is stable in $\text{CHCl}_3\text{-CH}_3\text{OH}$ for several days.

The sample is treated with hydroxylamine-hydrochloride to reduce cupric ions to cuprous ions. Sodium citrate is used to complex metallic ions that might precipitate when the pH is raised. The pH is adjusted to 4 to 6 with NH_4OH , a solution of neocuproine in methanol is added, and the resultant complex is extracted into CHCl_3 . After dilution of the CHCl_3 to an exact volume with CH_3OH , the absorbance of the solution is measured at 457 nm.

b. Interference: Large amounts of chromium and tin may interfere. Avoid interference from chromium by adding sulfurous acid to reduce chromate and complex chromic ion. In the presence of much tin or excessive amounts of other oxidizing ions, use up to 20 mL additional hydroxylamine-hydrochloride solution.

Cyanide, sulfide, and organic matter interfere but can be removed by a digestion procedure (see Section 3030).

c. Minimum detectable concentration: The minimum detectable concentration, corresponding to 0.01 absorbance or 98% transmittance, is 3 $\mu\text{g Cu}$ when a 1-cm cell is used and 0.6 $\mu\text{g Cu}$ when a 5-cm cell is used.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer*, for use at 457 nm, providing a light path of 1 cm or longer.

2. Selection of Method

The atomic absorption spectrometric methods (3111B and C), the inductively coupled plasma methods (3120 and 3125), and the neocuproine method (B) are recommended because of their freedom from interferences. The electrothermal atomic absorption method (3113B) also may be used with success with an appropriate matrix modifier. The bathocuproine method (C) may be used for potable waters.

3. Sampling and Storage

Copper ion tends to be adsorbed on the surface of sample containers. Therefore, analyze samples as soon as possible after collection. If storage is necessary, use 0.5 mL 1 + 1 HCl/100 mL sample, or acidify to pH <2 with HNO_3 , to prevent this adsorption.

2) *Filter photometer*, providing a light path of 1 cm or longer and equipped with a narrow-band violet filter having maximum transmittance in the range 450 to 460 nm.

b. Separatory funnels, 125-mL, Squibb form, with glass or TFE stopcock and stopper.

3. Reagents

a. Redistilled water, copper-free: Because most ordinary distilled water contains detectable amounts of copper, use redistilled water, prepared by distilling singly distilled water in a resistant-glass still, or distilled water passed through an ion-exchange unit, to prepare all reagents and dilutions.

b. Stock copper solution: To 200.0 mg polished electrolytic copper wire or foil in a 250-mL conical flask, add 10 mL water and 5 mL conc HNO_3 . After the reaction has slowed, warm gently to complete dissolution of the copper and boil to expel oxides of nitrogen, using precautions to avoid loss of copper. Cool, add about 50 mL water, transfer quantitatively to a 1-L volumetric flask, and dilute to the mark with water; 1 mL = 200 $\mu\text{g Cu}$.

c. Standard copper solution: Dilute 50.00 mL stock copper solution to 500 mL with water; 1.00 mL = 20.0 $\mu\text{g Cu}$.

d. Sulfuric acid, H_2SO_4 , conc.

e. Hydroxylamine-hydrochloride solution: Dissolve 50 g $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 450 mL water.

f. Sodium citrate solution: Dissolve 150 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ in 400 mL water. Add 5 mL $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution and 10 mL neocuproine reagent. Extract with 50 mL CHCl_3 to remove copper impurities and discard CHCl_3 layer.

g. Ammonium hydroxide, NH_4OH , 5*N*: Dilute 330 mL conc NH_4OH (28-29%) to 1000 mL with water. Store in a polyethylene bottle.

h. Congo red paper, or other pH test paper showing a color change in the pH range of 4 to 6.

i. Neocuproine reagent: Dissolve 100 mg 2,9-dimethyl-1,10-phenanthroline hemihydrate* in 100 mL methanol. This

* GFS Chemicals, Inc., Columbus, OH, or equivalent.

solution is stable under ordinary storage conditions for a month or more.

j. Chloroform, CHCl₃: Avoid or redistill material that comes in containers with metal-lined caps.

k. Methanol, CH₃OH, reagent grade.

l. Nitric acid, HNO₃, conc.

m. Hydrochloric acid, HCl, conc.

4. Procedure

a. Preparation of calibration curve: Pipet 50 mL water into a 125-mL separatory funnel for use as a reagent blank. Prepare standards by pipetting 1.00 to 10.00 mL (20.0 to 200 μg Cu) standard copper solution into a series of 125-mL separatory funnels, and dilute to 50 mL with water. Add 1 mL conc H₂SO₄ and use the extraction procedure given in ¶ 4*b* below.

Construct a calibration curve by plotting absorbance versus micrograms of copper.

To prepare a calibration curve for smaller amounts of copper, dilute 10.0 mL standard copper solution to 100 mL. Carry 1.00- to 10.00-mL volumes of this diluted standard through the previously described procedure, but use 5-cm cells to measure absorbance.

b. Treatment of sample: Transfer 100 mL sample to a 250-mL beaker, add 1 mL conc H₂SO₄ and 5 mL conc HNO₃. Add a few boiling chips and cautiously evaporate to dense white SO₃ fumes on a hot plate. If solution remains colored, cool, add another 5 mL conc HNO₃, and again evaporate to dense white fumes. Repeat, if necessary, until solution becomes colorless.

Cool, add about 80 mL water, and bring to a boil. Cool and filter into a 100-mL volumetric flask. Make up to 100 mL with water using mostly beaker and filter washings.

Pipet 50.0 mL or other suitable portion containing 4 to 200 μg Cu, from the solution obtained from preliminary treatment, into a 125-mL separatory funnel. Dilute, if necessary, to 50 mL with water. Add 5 mL NH₂OH · HCl solution and 10 mL sodium citrate solution, and mix thoroughly. Adjust pH to approximately

4 by adding 1-mL increments of NH₂OH until Congo red paper is just definitely red (or other suitable pH test paper indicates a value between 4 and 6).

Add 10 mL neocuproine reagent and 10 mL CHCl₃. Stopper and shake vigorously for 30 s or more to extract the copper-neocuproine complex into the CHCl₃. Let mixture separate into two layers and withdraw lower CHCl₃ layer into a 25-mL volumetric flask, taking care not to transfer any of the aqueous layer. Repeat extraction of the water layer with an additional 10 mL CHCl₃ and combine extracts. Dilute combined extracts to 25 mL with CH₃OH, stopper, and mix thoroughly.

Transfer an appropriate portion of extract to a suitable absorption cell (1 cm for 40 to 200 μg Cu; 5 cm for lesser amounts) and measure absorbance at 457 nm or with a 450- to 460-nm filter. Use a sample blank prepared by carrying 50 mL water through the complete digestion and analytical procedure.

Determine micrograms copper in final solution by reference to the appropriate calibration curve.

5. Calculation

$$\text{mg Cu/L} = \frac{\mu\text{g Cu (in 25 mL final volume)}}{\text{mL portion taken for extraction}}$$

6. Bibliography

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3500-Cu C. Bathocuproine Method

1. General Discussion

a. Principle: Cuprous ion forms a water-soluble orange-colored chelate with bathocuproine disulfonate (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disulfonic acid, disodium salt). While the color forms over the pH range 3.5 to 11.0, the recommended pH range is between 4 and 5. The sample is buffered at a pH of about 4.3 and reduced with hydroxylamine hydrochloride. The absorbance is measured at 484 nm. The method can be applied to copper concentrations up to at least 5 mg/L with a sensitivity of 20 $\mu\text{g/L}$.

b. Interference: The following substances can be tolerated with an error of less than $\pm 2\%$:

Substance	Concentration mg/L
Cations	
Aluminum	100
Beryllium	10
Cadmium	100
Calcium	1000
Chromium (III)	10
Cobalt (II)	5
Iron (II)	100
Iron (III)	100
Lithium	500
Magnesium	100
Manganese (II)	500
Nickel (II)	500

Substance	Concentration mg/L
Sodium	1000
Strontium	200
Thorium (IV)	100
Zinc	200
Anions	
Chlorate	1000
Chloride	1000
Fluoride	500
Nitrate	200
Nitrite	200
Orthophosphate	1000
Perchlorate	1000
Sulfate	1000
Compounds	
Residual chlorine	1
Linear alkylate sulfonate (LAS)	40

Cyanide, thiocyanate, persulfate, and EDTA also can interfere.

c. *Minimum detectable concentration:* 20 $\mu\text{g/L}$ with a 5-cm cell.

2. Apparatus

a. *Colorimetric equipment:* One of the following, with a light path of 1 to 5 cm (unless nessler tubes are used):

- 1) *Spectrophotometer*, for use at 484 nm.
- 2) *Filter photometer*, equipped with a blue-green filter exhibiting maximum light transmission near 484 nm.
- 3) *Nessler tubes*, matched, 100-mL, tall form.

b. *Acid-washed glassware:* Rinse all glassware with conc HCl and then with copper-free water.

3. Reagents

a. *Copper-free water:* See Method B, ¶ 3a.

b. *Stock copper solution:* Prepare as directed in Method B, ¶ 3b, but use 20.00 mg copper wire or foil; 1.00 mL = 20.00 μg Cu.

c. *Standard copper solution:* Dilute 250 mL stock copper solution to 1000 mL with water; 1.00 mL = 5.00 μg Cu. Prepare daily.

d. *Hydrochloric acid*, HCl, 1 + 1.

e. *Hydroxylamine hydrochloride solution:* See Method B, ¶ 3e.
f. *Sodium citrate solution:* Dissolve 300 g $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ in water and make up to 1000 mL.

g. *Disodium bathocuproine disulfonate solution:* Dissolve 1.000 g $\text{C}_{12}\text{H}_4\text{N}_2(\text{CH}_3)_2(\text{C}_6\text{H}_4)_2(\text{SO}_3\text{Na})_2$ in water and make up to 1000 mL.

4. Procedure

Pipet 50.0 mL sample, or a suitable portion diluted to 50.0 mL, into a 250-mL erlenmeyer flask. In separate 250-mL erlenmeyer flasks, prepare a 50.0-mL water blank and a series of 50.0-mL copper standards containing 5.0, 10.0, 15.0, 20.0, and 25.0 μg Cu. To sample, blank, and standards add, mixing after each addition, 1.00 mL 1 + 1 HCl, 5.00 mL $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution, 5.00 mL sodium citrate solution, and 5.00 mL disodium bathocuproine disulfonate solution. Transfer to cells and read sample absorbance against the blank at 484 nm. Plot absorbance against micrograms Cu in standards for the calibration curve. Estimate concentration from the calibration curve.

5. Calculation

$$\text{mg Cu/L} = \frac{\mu\text{g Cu (in 66 mL final volume)}}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 1000 μg Cu/L, 500 μg Al/L, 50 μg Cd/L, 110 μg Cr/L, 300 μg Fe/L, 70 μg Pb/L, 50 μg Mn/L, 150 μg Ag/L, and 650 μg Zn/L was analyzed in 33 laboratories by the bathocuproine method, with a relative standard deviation of 4.1% and a relative error of 0.3%.

7. Bibliography

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