

# Copper, atomic absorption spectrometric, chelation-extraction

## Parameters and Codes:

Copper, dissolved, I-1271-85 ( $\mu\text{g/L}$  as Cu): 01040  
Copper, total recoverable, I-3271-85 ( $\mu\text{g/L}$  as Cu): 01042  
Copper, suspended recoverable, I-7271-85 ( $\mu\text{g/L}$  as Cu): 01041

### 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 50  $\mu\text{g/L}$  of copper. Sample solutions containing more than 50  $\mu\text{g/L}$  need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

1.2 Suspended recoverable copper is calculated by subtracting dissolved copper from total recoverable copper.

1.3 Total recoverable copper in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 25,000  $\mu\text{g/L}$ , determine copper by the atomic absorption spectrometric direct method.

### 2. Summary of method

Copper is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer.

### 3. Interferences

Concentrations of iron greater than 25,000  $\mu\text{g/L}$  interfere by suppressing the copper absorption.

### 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating	-----	Ultraviolet
Wavelength	-----	324.7 nm
Source (hollow-cathode lamp)	-----	Copper
Oxidant	-----	Air
Fuel	-----	Acetylene
Type of flame	-----	Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

### 5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Copper standard solution I*, 1.00 mL=100  $\mu\text{g}$  Cu: Dissolve 0.1252 g CuO in a minimum amount of dilute  $\text{HNO}_3$ . Heat to increase rate of dissolution. Add 10.0 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.4 *Copper standard solution II*, 1.00 mL=1.00  $\mu\text{g}$  Cu: Dilute 10.0 mL copper standard solution I and 1 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.5 *Methyl isobutyl ketone (MIBK)*.

5.6 *Potassium hydroxide*, 10M: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide, 2.5M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1. Alternatively, a 2.5M  $\text{NH}_4\text{OH}$  solution may be used. Add 167 mL concentrated  $\text{NH}_4\text{OH}$  (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) to 1 L of demineralized water.

## 6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute  $\text{HNO}_3$  (1+9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 5.0  $\mu\text{g}$  Cu (100 mL max) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.3 Prepare a blank with 1.5 mL concentrated  $\text{HNO}_3$  per liter of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 with 2.5M KOH (NOTE 2 and NOTE 3). Shake for 3 min.

NOTE 2. For water-suspended sediment samples that have been digested, add 1 to 2 mL 10M KOH or concentrated  $\text{NH}_4\text{OH}$  (sp gr 0.90) before pH adjustment.

NOTE 3. If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5 Add 2.5 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8 Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

## 7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable copper in each sample from the digital display or printer. Dilute those samples containing copper concentrations that exceed the working range of the method; repeat the chelation-extraction, and multiply by the proper dilution factors.

7.2 To determine the micrograms per liter of suspended recoverable copper, subtract dissolved-copper concentration from total-recoverable-copper concentration.

## 8. Report

Report copper, dissolved (01040), total-recoverable (01042), and suspended-recoverable (01041), concentrations as follows: less than 10  $\mu\text{g/L}$ , nearest microgram per liter; 10  $\mu\text{g/L}$  and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved copper for eight samples within the range of 18.5 to 403  $\mu\text{g/L}$  may be expressed as follows:

$$S_T = 0.084X + 2.57$$

where

$S_T$  = overall precision, micrograms per liter, and

$X$  = concentration of copper, micrograms per liter.

The correlation coefficient is 0.8156.

9.2 Precision for dissolved copper for four of the eight samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean ( $\mu\text{g/L}$ )	Relative standard deviation (percent)
4	18.5	14
3	100	0
3	153	21
3	403	8

9.3 It is estimated that the percent relative standard deviation for total-recoverable and suspended recoverable copper will be greater than that reported for dissolved copper.