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जल और अपशिष्ट जल के लिए नमूने लेने एवं परीक्षण (भौतिक एवं रसायन) की पद्धतियां

भाग 42 ताँबा

(*पहला पुनरीक्षण*)

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 42 COPPER

(First Revision)

Fourth Reprint SEPTEMBER 2007
(Including Amendment No. 1)

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AMENDMENT NO. 1 MAY 2004
TO
IS 3025 (PART 42) : 1992 METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 42 COPPER

(First Revision)

(*Page* 1, *clause* 5.2, *line* 3) — Insert the words 'suspended solids' in between the words 'organic matter' and 'sulphide'.

(CHD 32)

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Environmental Protection Sectional Committee, CHD 012

FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Environmental Protection Sectional Committee had been approved by the Chemical Division Council.

Copper is found mainly as a sulphide, oxide or carbonate in the minerals. Copper enters the water system through mineral dissolution, industrial effluents, because of its use as algicide and insecticide and through corrosion of copper alloy water distribution pipes. It may occur in simple ionic form or in one of many complexes with groups, such as cyanides, chlorides, ammonia or organic ligands. The test for copper is essential because dissolved copper salts even in low concentrations are poisonous to some biota. Desirable limit for copper in potable water is 0·05 mg/l maximum which can be relaxed in the absence of better alternate source to 1·5 mg/l.

In the preparation of this standard, considerable assistance has been derived from American Society for Testing and Materials, USA (*ASTM Annual Book Section 11, 1983*).

In reporting th results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 42 COPPER

(First Revision)

1 SCOPE

1.1 This standard prescribes four methods for determination of copper as follows:

a) Neocuproine method,
b) Atomic absorption method (direct),
c) Atomic absorption method (chelation — extraction), and
d) Differential pulse anodic stripping voltammetry.

1.2 The choice of the method depends upon the concentration range and interference. When the concentration levels are below 500 g/l, pre-concentration is carried out either by chelation and extraction prior to atomic absorption spectrophotometer (AAS) or by depositing as in differential pulse anodic stripping voltammetry method. For dissolved copper content filteration through 0·45 µm membrane filter is required.

2 REFERENCES

2.1 The following Indian Standards are the necessary adjuncts to this standard:

IS No.	*Title*
3025 (Part 1) : 1986	Methods of sampling and test (physical and chemical) for water and wastewater: Part 1 Sampling
7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents: Part 1
7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents: Part 2

3 SAMPLING AND PRESERVATION

3.1 The sampling and storage shall be done as prescribed in IS 3025 (Part 1) : 1986. The sample bottles should be cleaned thoroughly with dilute nitric acid (6 N) prior to the final rinsing with water. The water samples should be collected and stored for 24 h preferably in polypropylene or chemically resistant glass containers. For preservation, the samples should be acidified with concentrated nitric acid (2 ml of AR grade nitric acid to 1 litre just to bring down the *p*H below 2). Unacidified samples should be analysed on the same day while the acidified samples may be stored for a few days in a refrigerator.

4 QUALITY OF REAGENTS

4.1 Unless specified otherwise, pure chemicals shall be used.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4.2 Double distilled water with a specific conductivity less than 1 µs/cm shall be used for preparing the standard and reagent solutions.

5 NEOCUPROINE METHOD

5.1 Principle

Copper (II) is reduced to copper (I) by hydroxyl amine hydrochloride and the *p*H of the solution is adjusted to 5 by sodium citrate solution. Copper (I) forms a soluble yellow complex with 2, 9-dimethyl-1, 10-phenanthroline (neocuproine) suitable for spectrophotometric measurement. This method is applicable in the concentration range of 0·05 to 5 mg/l of copper.

5.2 Interferences

Chromium interferes when its concentration exceeds 5 times that of copper. The interference from organic matter, sulphide, cyanide and chromium can be eliminated by a preliminary sample treatment as given in **5.5.1**. The other commonly present ions do not interfere.

5.3 Apparatus

5.3.1 *Spectrophotometer* — for use at 457 nm with 1 cm cell.

5.4 Reagents

5.4.1 *Ammonium Hydroxide* — Specific gravity 0·90.

5.4.2 *Chloroform* — AR grade.

5.4.3 *Hydrochloric Acid* — Concentrated.

5.4.4 *Hydroxylamine Hydrochloride Solution*

Dissolve 40 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) in 200 ml of water.

5.4.5 *Isopropyl Alcohol*

5.4.6 *Neocuproine Solution*

Dissolve 0·1 g of neocuproine in 50 ml of isopropyl alcohol. Dilute to 100 ml with double distilled water.

5.4.7 *Nitric Acid* — Concentrated.

5.4.8 *Sulphuric Acid* — Concentrated.

5.4.9 *Sodium Citrate Solution*

Dissolve 250 g of hydrated sodium citrate ($Na_3C_6H_5O_7.2H_2O$) in water and make up to 1 000 ml. Add 10 ml each of neocuproine solution and hydroxy lamine hydrochloride solution. Any impurities of copper can be removed by extraction with chloroform, discarding the chloroform layer.

5.4.10 *Copper (II) Solutions*

5.4.10.1 *Stock copper (II) solution*

Dissolve 0·2 g of pure copper metal by warming with 6 ml of 1 : 1 nitric acid. Add 1 ml of concentrated sulphuric acid and evaporate the solution to dryness. Dilute the solution to 1 litre with distilled water. 1 ml = 200 μg of Copper (II).

5.4.10.2 *Intermediate copper (II) solution*

Dilute 100 ml of stock solution to 1 litre with distilled water. 1 ml = 20 μg/l.

5.4.10.3 *Standard copper (II) solution*

Dilute 1 ml of intermediate stock solution to 50 ml with distilled water. 1 ml = 0·4 μg/l. Prepare diluted solutions daily.

5.5 Procedure

5.5.1 If interfering substances are present add 1 ml of concentrated sulphuric acid and 5 ml of concentrated nitric acid. Evaporate the sample to dense white sulphur trioxide fumes on a hot plate. Repeat the treatment with 5 ml of concentrated nitric acid and 5 ml of hydrogen peroxide and evaporate the solution to complete dryness. Dissolve the residue with 80 ml of water, boil, cool and filter. Adjust the *p*H with dropwise addition of ammonium hydroxide to 4 to 6. Add 0·2 ml of hydrochloric acid and dilute to 100 ml. If no interfering substance is present, just boil the acidified sample and cool.

5.5.2 *Extraction*

Transfer 50 ml of the acidified sample or filtrate (5.5.1) to a 125 ml separating funnel. Add 5 ml of hydroxylamine-hydrochloride solution, 10 ml of sodium citrate solution and 10 ml of neocuproine solution. Shake well. Add 20 ml of chloroform and shake for 1 minute. Allow the aqueous and chloroform layers to separate. Collect the chloroform layer in a dry flask. Repeat with separate 20 ml aliquot of chloroform. Combine the extracts and dilute to 50 ml with isopropyl alcohol. Prepare a reagent blank by treating 50 ml of double distilled water in the same way as described above.

5.5.3 Measure the optical density of the sample solution at 457 nm against the reagent blank. Treat 50 ml portions of standard solutions containing 0·05, 0·1, 0·5, 1·0, 5·0 mg/l of copper as above. Plot absorbance versus copper concentration (mg/l) for the standards to get a calibration graph. Read the concentration of copper in the sample from the calibration graph.

5.6 Calculation

$$\text{Copper, mg/l} = \frac{M}{V} \times 1\,000$$

where

M = mass in mg of copper in the sample, and

V = volume of sample in ml.

6 ATOMIC ABSORPTION METHOD (DIRECT)

6.1 Principle

The copper content of the sample is determined by atomic absorption spectrophotometry. For dissolved copper, the filtered sample is directly aspirated into the atomizer.

For total recoverable copper, an acid digestion procedure is carried out prior to aspiration of the sample. This method is applicable in the range of 0·02 to 5 mg/l.

6.2 Interferences

Cadmium, lead, nickel, zinc, cobalt, manganese and chromium up to 10 mg/l do not interfere. Alkali and alkaline earth metals can be tolerated up to 5 000 mg. Iron does not interfere upto 1 000 mg/l.

6.3 Apparatus

6.3.1 *Atomic Absorption Spectrophotometer* — with air-acetylene flame.

6.3.2 *Copper Hollow Cathode Lamp* — for use at 324·7 nm.

6.4 Reagents

6.4.1 *Hydrochloric Acid* — Concentrated.

6.4.2 *Nitric Acid* — Concentrated.

6.4.3 *Dilute Nitric Acid* — 1 : 500.

6.4.4 *Dilute Sulphuric Acid* — 1 : 1.

6.4.5 *Copper (II) Solutions*

6.4.5.1 *Stock copper (II) solution*

Dissolve 1·0 g of pure copper metal in 30 ml of (1 : 1) nitric acid and add 4 ml of (1 : 1) sulphuric acid and heat until sulphur trioxide fumes evolve. Cool the solution and dilute to 1 litre with distilled water. 1 ml = 1·0 mg of copper.

6.4.5.2 *Standard copper (II) solution*

Dilute 100 ml of copper stock solution to 1 litre with distilled water. 1 ml = 0·1 mg of copper.

6.5 Procedure

6.5.1 If total recoverable copper is to be determined, add 5 ml of concentrated hydrochloric acid and evaporate the solution to 15 to 20 ml. Cool and filter the sample through acid washed filter paper. Make up to 100 ml in a volumetric flask, aspirate the solution and measure the absorbance at 324·7 nm using copper hollow — cathode lamp. Aspirate nitric acid (1 : 500) prior to sample aspiration.

6.5.2 Prepare a reagent blank and series of standards containing 0, 0·02, 0·1, 0·5, 1, 2, 5 mg/l of copper by diluting a suitable volume of the standard solution with 100 ml of nitric acid (1 : 500) and repeat as above. Asprirate the solutions and measure the absorbance.

6.6 Calculations

Construct a standard calibration graph by plotting the absorbance versus copper concentration (mg/l) for each standard. Read the concentration of the sample from the graph:

$$\text{Copper, mg/l} = \frac{M}{V} \times 1\,000$$

where

M = mass (in g) of copper in the sample, and

V = volume of sample in ml.

7 ATOMIC ABSORPTION METHOD (CHELATION-EXTRACTION)

7.1 Principle

Copper (II) is chelated with pyrrolidine dithiocarbamic acid and extracted with MIBK. The extract is treated with hot nitric acid after evaporating to dryness, then dissolved in hydrochloric acid and diluted with water. An aliquot is aspirated into the air-acetylene flame of the spectrophotometer. For total recoverable copper an acid digestion procedure is carried out prior to aspiration of the sample. This method is applicable for the concentration range of 2 to 500 ug/l.

7.2 Interference — Same as in **6.2**.

7.3 Apparatus — Same as in **6.3**.

7.4 Reagents

7.4.1 *Hydrochloric Acid* — Concentrated.

7.4.2 *Dilute Hydrochloric Acid* — 1 : 2.

7.4.3 *Nitric Acid* — Concentrated.

7.4.4 *Pyrrolidine Dithiocarbamic Acid — Methyl isobutyl ketone (MIBK) reagent*

Mix 36 ml of pyrrolicine with 1 litre of MIBK. Cool and add 30 ml of carbon disulphide in small fractions with continuous stirring. Dilute with 2 litres of MIBK. Store in a cool and dark place. The reagent so prepared is stable for at least six months.

NOTE — As components of this mixture are highly toxic and flammable, prepare and use in a fumehood.

7.4.5 *Sodium Hydroxide Solution*

Dissolve 100 g of sodium hydroxide in distilled water and dilute to 1 litre.

7.4.6 *Methyl isobutyl ketone (MIBK)*

Reagent grade for trace analysis purify MIBK by redistillation or by subboiling distillation.

7.4.6.1 *Water standard MIBK*

Mix one part of purified MIBK with one part of water in a separatory funnel. Shake 30 times and let separate. Discard aqueous layer. Save MIBK layer.

7.4.7 *Bromophenol Blue Indicator Solution*

Dissolve 0·1 g of bromophenol blue in 100 ml of 50 percent ethanol or isopropanol.

7.4.8 *Copper (II) Solutions*

7.4.8.1 *Stock copper (II) solution* — Same as in **6.4.5.1**.

7.4.8.2 *Intermediate copper (II) solution*

Add 1 ml of concentrated nitric acid to 10 ml of stock solution and dilute to 1 litre with distilled water. 1 ml = 0·01 mg of copper.

7.4.8.3 *Standard copper (II) solution*

Dilute 10 ml of copper intermediate solution to 100 ml with distilled water. Prepare daily for use. 1 ml = 1 μg of copper.

7.5 Procedure

7.5.1 If total recoverable copper is to be determined, add 5 ml of concentrated hydrochloric acid and evaporate the solution to 15 to 20 ml. Cool and filter the sample through acid washed filter paper. Make up to 100 ml in a volumetric flask. Add 2 drops of bromophenol blue indicator solution and mix. Adjust the *p*H by adding sodium hydroxide solution till a blue colour persists. Add dilute hydrochloric acid (1 : 50) drop by drop until the colour just disappears. Then add 2·5 ml of dilute hydrochloric acid to bring the *p*H to 2·3 to 2·5. Add 10 ml of pyrrolidine dithiocarbamic acid-MIBK reagent and shake well. After the phases separate out, collect the MIBK phase by taking care to avoid any trace of water in the flask. Repeat the extraction twice with 6 to 7 ml of MIBK and combine the extracts. Aspirate the organic extract directly into the flame (Zeroing instrument on a water staturated MIBK blank) and record absorbances. To avoid problems associated with instability of extracted metal complexes determine immediately after extraction. Evaporate the solution just to dryness and dissolve the residue by dropwise addition of 2 ml of concentrated nitric acid by holding the beaker at an angle. Again evaporate to dryness and add 2 ml of hydrochloric acid (1 : 2) and heat for 1 minute. Cool and make up the solution in a 10 ml standard flask. Aspirate the sample and measure the absorbance.

7.5.2 Prepare a reagent blank and a series of standards containing 0, 10, 20, 50, 100, 200, 500 μg/l of copper by diluting a suitable volume of the standards solution. Treat the standards in the same manner as the sample. Aspirate the MIBK extracts and measure the absorbance.

7.6 Calculation

7.6.1 Construct a standard calibration graph by plotting the absorbance versus the concentration of copper (μg/l). Read the concentration of the sample from the curve.

$$\text{Copper, } \mu g/l = \frac{M}{V} \times 1\,000$$

where

M = mass in μg of copper in the sample
V = volume of the sample in ml.

8 DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

8.1 Scope and Application

Copper is deposited on a hanging mercury drop at a negative potential of −0·4 V versus saturated calomel electrode. Then the copper is stripped back into the solution by applying a positive potential scan. The anodic current peak which is measured represents the copper concentration in the sample. For total dissolved copper the sample is filtered through a Whatman No. 40 filter paper prior to acidification analysis.

This method is applicable in the concentration range of 0·1 — 100 μg/l of copper.

8.2 Interferences

Iron interferes when present at levels greater than the copper. This can be overcome by subtracting the anodic peak current for a voltammogram without deposition from that for the stripping voltammogram. The presence of any neighbouring stripping peaks which is less than 100 mV from that of copper will interfere.

8.3 Apparatus

8.3.1 Polarographic instrumentation capable of performing differential pulse work.

8.3.2 *Hanging Mercury Drop Electrode*

8.3.3 *Platinum Counter Electrode*

8.3.4 *Saturated Calomel Reference Electrode*

8.3.5 *Magnetic Stirrer Control Unit, Stirring Bar*

8.4 Reagents

8.4.1 *Hydrochloric acid*—concentrated; spectrograde.

8.4.2 *Nitric Acid* — concentrated; spectrograde.

8.4.3 *Dilute Sulphuric Acid* — 1 : 1.

8.4.4 *Dilute Nitric Acid* — 1 : 1.

8.4.5 *Copper (II) Solutions*

8.4.5.1 *Stock copper (II) solution* — Same as in **6.4.5.1.**

8.4.5.2 *Intermediate copper (II) solution*

Dilute 100 ml of stock solution to be 1 litre with distilled water.

8.4.5.3 *Standard copper (II) solution* — Same as in **7.4.8.3.**

8.4.6 *Amalgamated Zinc*

Cover 100 g of granular zinc with water and add 2 drops of concentrated hydrochloric acid. Then add 5 to 8 drops of mercury with continuous shaking.

8.4.7 *Purified Nitrogen*

Boil 2 g of ammonium meta vanadate with 25 ml of concentrated hydrochloric acid. Dilute 250 ml and transfer to the scrubber. Add 10 to 15 g of amalgamated zinc. Pass nitrogen gas through the scrubber for removal of oxygen and through distilled water for washing any traces of scrubber chemicals (Fig. 1).

8.5 Procedure

8.5.1 Clean all the glassware and the voltammetric cells by soaking them overnight in concentrated nitric acid and rinsing them thoroughly with distilled water. If the total dissolved copper alone is to be determined, the sample should be filtered through Whatman No. 40 filter paper. For total recoverable copper, digest the sample with 3 ml each of concentrated hydrocloric acid and nitric acid. Evaporate the solution to 15 to 20 ml. Cool and make up to 100 ml in a volumetric flask. Take 10 ml of the sample in the polarographic cell and de-aerate for 15 minutes. The cell should be covered with nitrogen gas during the experiment (Fig. 2). Generate a new droplet of mercury and put the stirrer on. Connect the cell and deposit at —0·40 V versus saturated calomel electrode for 3 minutes. Stop the stirrer and wait for 30 seconds. Start the anodic scan with the following settings:

Initial potential : — 0·4 V *vs* saturated calomel electrode (SLE)
Scan rate : 5 mV/s
Scan direction : +
Modulation amplitude : 25 mV
Current range : 1 — 10 µA
Droptime : 5 sec
Display direction : '—'
Low pass filter : Off position
Mode : Differential pulse
Scan range : 0·75 V

Measuse the current peak height (I_1). Add 20 µl of standard copper (II) solution and de-aerate for 5 minutes. Repeat as above. Measure the current peak height (I_2).

8.6 Calculation

$$\text{Copper, } \mu g/l = \frac{I_1 \; V \; C_{std}}{I_2 \, v + (I_2 - I_1) V} \times 1\,000$$

where

I_1 = current peak height for sample,
I_2 = current peak height for sample + standard,
v = volume of standard added (20 µl),
V = volume of the sample solution in ml, and
C_{std} = concentration of the standard solution added.

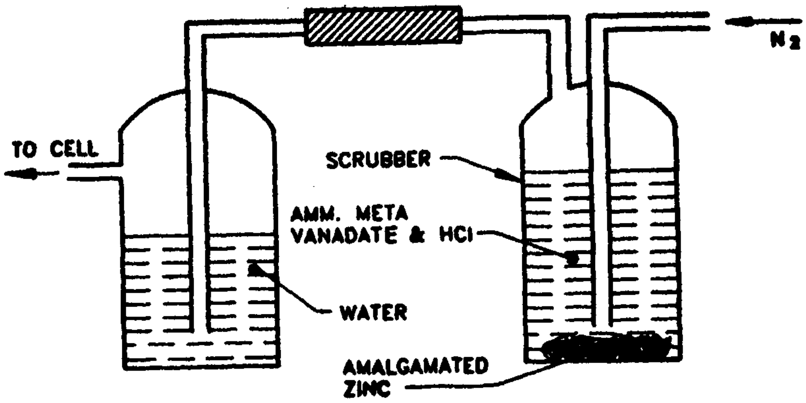

FIG. 1 SCRUBBER ASSEMBLY FOR NITROGEN PURIFICATION

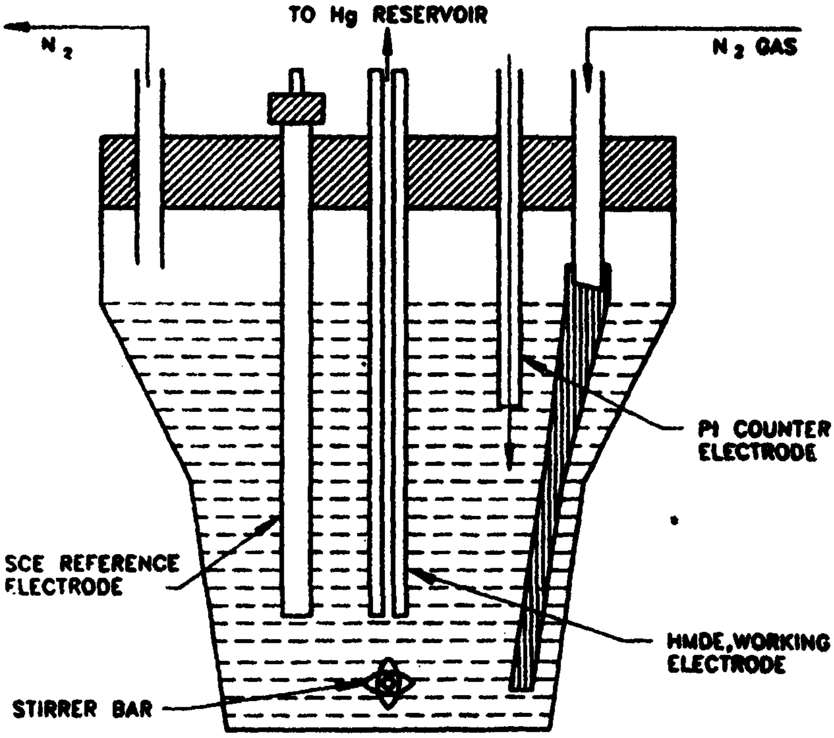

FIG. 2 VOLTAMMETRIC CELL ASSEMBLY

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Review of Indian Standards

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