(Reaffirmed 1998)

भारतीय मानक

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

भाग 41 कैडमियम

(पहला पुनरीक्षण)

Indian Standard

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

PART 41 CADMIUM

(First Revision)

First Reprint OCTOBER 1996

UDC 628·1/·3 : 543 [546·48]

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September 1992 **Price Group 3**

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.

Cadmium is highly toxic and has been implicated in some cases of poisoning through food. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. Cadmium may enter water as a result of industrial discharges or the deterioration of galvanized water supply pipe. Desirable limit for cadmium in drinking water is 0·01 mg/l beyond which the water becomes toxic and no relaxation of this limit is allowed. The test for cadmium is, therefore, essential.

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

In reporting the 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 41 CADMIUM

(First Revision)

1 SCOPE

1.1 This standard prescribes the following three methods for determination of cadmium:

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

1.2 The choice of the method depends upon the concentration range and interference levels. Determination using atomic absorption method can be done either directly or by chelation and extraction prior to atomic absorption spectrophotometer determination.

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standards:

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

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 ATOMIC ABSORPTION METHOD (DIRECT)

5.1 Principle

The cadmium content of the sample is determined by directly aspirating the sample into the flame of an atomic absorption spectrophotometer. The absorbance is measured at 228·8 nm using a cadmium hollow-cathode lamp. This method is applicable in the concentration range of 0·05 to 2 mg/l. However, the concentration range will vary with the sensitivity of the instrument used.

5.2 Interferences

Nickel, lead, copper zinc, cobalt and chromium do not interfere up to 10 mg/l. Alkali and alkaline earth metals can be tolerated up to 5 000 mg/l. Iron does not interfere up to 4 000 mg/l.

5.3 Apparatus

5.3.1 Atomic absorption spectrophotometer with air-acetylene flame.

5.3.2 Cadmium hollow-cathode lamp or multi-element hollow-cathode lamp for use at 228·8 nm.

5.4 Reagents

5.4.1 *Hydrochloric Acid* — Concentrated.

5.4.2 *Nitric Acid* — Concentrated.

5.4.3 *Nitric Acid* — Diluted (1 : 499).

5.4.4 *Cadmium Solutions*

5.4.4.1 *Stock cadmium solution*

Dissolve 1·0 g of pure cadmium metal in minimum quantity of concentrated nitric acid and dilute to 1 litre with distilled water (1 ml= 1 mg of Cd).

5.4.4.2 *Standard cadmium solution*

Add 1 ml of concentrated nitric acid to 100 ml of the cadmium stock solution (**5.4.4.1**) and dilute to 1 litre with distilled water.

5.5 Procedure

5.5.1 To 100 ml portion of the acidified sample add 5 ml of concentrated hydrochloric acid and evaporate to 20 ml. Cool and filter the sample and make up to 100 ml in a standard flask. If only dissolved cadmium is to be determined, filter 100 ml of the sample and acidify with 0·1 ml of concentrated hydrochloric acid. Aspirate the sample solution and measure the absorbance at 228·8 nm. Aspirate nitric acid (1 : 499) prior to sample aspiration.

5.5.2 Prepare a reagent blank and a series of 100 ml standards containing 0·0, 0·05, 0·1, 0·5, 1 and 2 mg/l of cadmium by diluting a suitable volume of the standard solution with dilute nitric acid and repeat as above. Aspirate the solutions and measure the absorbance.

5.6 Calculation

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

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

where

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

V = volume of the sample in ml.

6 ATOMIC ABSORPTION METHOD (CHELATION AND EXTRACTION)

6.1 Principle

Cadmium is chelated with pyrrolidine dithio carbamic acid and extracted with methyl isobutyl ketone (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 cadmium, an acid digestion procedure is carried out prior to aspiration of the sample.

This method is applicable in the concentration range of 5 to 200 µg/l cadmium.

6.2 Interferences — Same as in **5.2.**

6.3 Apparatus

6.3.1 Same as in **5.3.**

6.4 Reagents

6.4.1 *Hydrochloric Acid* — Concentrated.

6.4.2 *Nitric Acid* — Concentrated.

6.4.3 *Dilute Nitric Acid* — 1 : 499.

6.4.4 *Cadmium Solutions*

6.4.4.1 *Stock cadmium solution* — Prepare as in **5.4.4.1.**

6.4.4.2 *Intermediate cadmium solution*

Add 1 ml of concentrated nitric acid to 50 ml of stock solution and dilute to 1 litre with water. 1 ml =50 µg of cadmium.

6.4.4.3 *Standard cadmium solution*

To 10 ml of cadmium intermediate solution add 1 ml of concentrated nitric acid and dilute to 1 litre with water. 1 ml = 0·5 µg of cadmium.

6.4.5 *Sodium Hydroxide Solution*

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

6.4.6 *Methyl Isobutyl Ketone (MIBK)* — Reagent grade.

For trace analysis purify MIBK by redistillation or by sub-boiling distillation.

6.4.6.1 *Water saturated 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.

6.4.7 *Bromophenol Blue Indicator Solution*

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

6.4.8 *Pyrrolidine Dithiocarbamic Acid — Methyl isobutyl Ketone (MIBK) Reagent*

Mix 36 ml of pyrrolidine with 1 litre of MIBK. Cool the solution 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.

6.5 Procedure

6.5.1 If total recoverable cadmium 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 : 49) 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, 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 till the MIBK layer becomes colourless. Combine the extracts. Aspirate the organic extract directly into the flame (zeroing instrument on a water saturated MIBK blank) and record absorbance. 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.

NOTE — Evaporation should be carried out at low heat using hot plate to avoid any losses due to volatilization of cadmium.

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

6.6 Calculation

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

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

where

M = mass of cadmium in µg in the sample , and
V = volume of sample in ml.

7 DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

7.1 Principle

Cadmium is deposited on a hanging mercury drop electrode at a negative potential of −0·8 V versus saturated calomel electrode. Then the cadmium is stripped back into the solution by applying a positive potential scan. The anodic current peak which is measured is representative of the cadmium concentration in the sample. For total dissolved cadmium the sample is filtered through Whatman No. 40 filter paper prior to acidification and analysis. This method is applicable in the concentration range of 0.1-100 µg/l.

7.2 Interferences

Selenium interferes when its concentration exceeds 50 µg/l. This can be overcome by adding ascorbic acid which reduces selenium (IV) to selenium metal. Iron (III) interferes when present at levels greater than cadmium. However, this can be overcome by warming the solution with hydroxylamine. The presence of any other neighbouring stripping peaks which is less than 100 mV from that of cadmium will interfere.

7.3 Apparatus

7.3.1 Polarographic instrumentation capable of performing differential pulse work.

7.3.2 *Hanging Mercury Drop Electrode*

7.3.3 *Platinum Counter Electrode*

7.3.4 *Saturated Calomel Reference Electrode (SCE)*

7.3.5 *Magnetic Stirrer Control Unit, Stirring Bar*

7.4 Reagents

7.4.1 *Hydrochloric Acid* – Concentrated; spectrograde.

7.4.2 *Nitric Acid* — Concentrated; spectrograde.

7.4.3 *Hydroxylamine Solution — 100 g/l*

Dissolve 5 g of hydroxylamine hydrochloride in 50 ml of water.

7.4.4 *Dilute Nitric Acid* — 1 : 1

7.4.5 *Ascorbic Acid — 100 mg/l*

Dissolve 10 g of L-ascorbic acid in 100 ml of water.

7.4.6 *Cadmium Solutions*

7.4.6.1 *Stock cadmium solution*

Dissolve 1·0 of pure cadmium metal by warming with 10 ml of concentrated hydrochloric acid and 30 ml of 1 : 1 nitric acid. Dilute to 1 litre with distilled water.

7.4.6.2 *Intermediate cadmium solution*

Add 1 ml of concentrated nitric acid to 10 ml of stock solution and dilute to 1 litre with distilled water.

7.4.6.3 *Standard cadmium solution*

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

7.4.7 *Amalgamated Zinc*

Cover 10 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.

7.4.8 *Purified Nitrogen*

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

7.5 Procedure

Clean all the glassware and the voltammetric cells by soaking them overnight in concentrated nitric acid and rinsing them thoroughly with water. Add 1 ml of hydroxylamine solution. Warm for 15 minutes to reduce the ferric concentration. Add 1 ml of ascorbic acid. Evaporate gently. Cool and make up to 100 ml. If total dissolved cadmium alone is to be determined, the sample should be filtered through 0·45 μm membrane filter paper. For total recoverable cadmium, digest the sample with 3 ml each of concentrated hydrochloric acid and nitric acid. Evaporate the solution to 15 to 20 ml. Cool and make up to 100 ml in a standard 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 −0·80 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	−0·80 V vs saturated calomel electrode (SCE)
Scan rate	5 mV
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

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

7.6 Calculation

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

I_1 = current peak height for sample,

I_2 = current peak height for sample and standard,

v = volume of standard added (20 μl),

V = volume of the sample solution in ml, and

Cstd = concentration of the standard solution added.

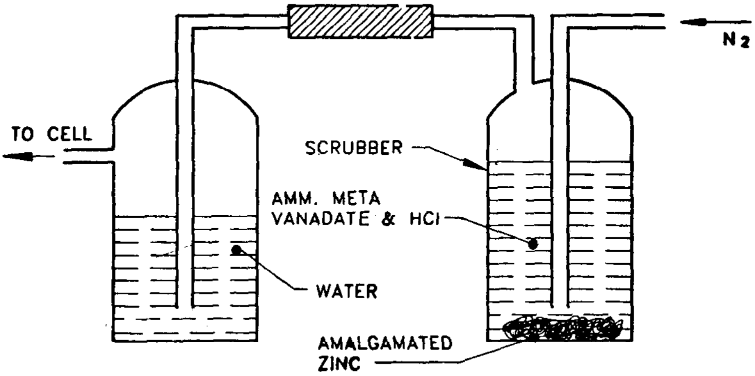

FIG. 1 SCRUBBER ASSEMBLY FOR NITROGEN PURIFICATION

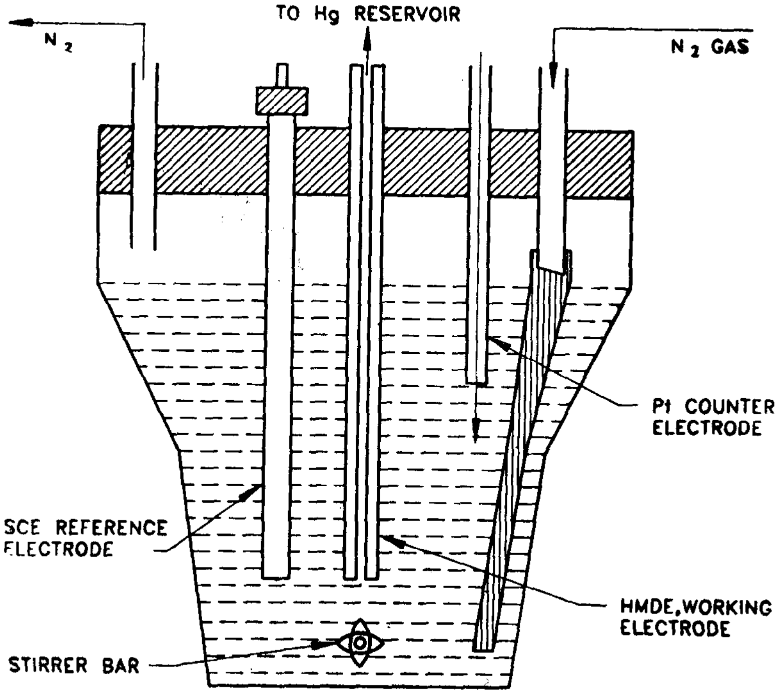

FIG. 2 VOLTAMMETRIC CELL ASSEMBLY

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Review of Indian Standards

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This Indian Standard has been developed from Doc : No. **CHD 12 (0055)**

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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Printed at Dee Kay Printers, New Delhi-110015, India.