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भाग 48 पारा

(पहला पुनरीक्षण)

Indian Standard

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

PART 48 MERCURY

(First Revision)

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Price Group 3

Environmental Protection Sectional Committee, CHD 012

FOREWORD

This Indian Standard (Part 48) (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.

Organic and inorganic mercury salts are very toxic and their presence in the environment, especially in water, should be monitored. Therefore, it is desirable to ascertain the limit of mercury present in water and wastewater. In the preparation of this standard, considerable assistance has been derived from Standard Methods for Examination of Water and Wastewater, 16th Edition, 1985.

The technical committee responsible for formulation of IS 2488 and IS 3025 : 1964 decided to revise all the parts covered under them and publish as separate parts.

This standard supersedes 7 of IS 2488 (Part 5) : 1976 'Methods of sampling and test for industrial effluents, Part 5.

The composition of the technical committee responsible for the formulation of this Indian Standard is given in Annex A.

In reporting the result 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 48 MERCURY

(First Revision)

1 SCOPE

This standard prescribes two methods for the determination of mercury in water and wastewater.

a) Cold vapour atomic absorption spectrophotometric method, and

b) Colorimetric dithizone method.

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard:

IS No.	*Title*
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 TERMINOLOGY

For the purpose of this standard, definitions given in IS 7022 (Part 1) : 1973 and IS 7022 (Part 2) : 1979 shall apply.

4 SAMPLE PRESERVATION

The sampling bottles should be cleaned thoroughly with dilute nitric acid (6 N) prior to final rinsing with water. The water samples should be collected and stored preferably in polypropylene or chemically resistant glass containers. For preservation, the sample should be acidified with concentrated nitric acid (2 ml of AR grade nitric acid in one litre of the sample just to bring down the *p*H below 2). For dissolved mercury, filter the sample in the field and acidify the filtrate with nitric acid to a *p*H of 2 or lower.

NOTE — Avoid excess nitric acid. Add 5 ml of 0·1 N iodine solution to avoid losses of volatile organo mercury components during handling and digestion of samples.

5 COLD VAPOUR ATOMIC ABSORPTION SPECTROMETRY

5.1 Principle

The flameless atomic absorption procedure is a physical method based on the absorption of radiation at 253·7 nm by mercury vapour. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapour passes through a cell positioned in the light path of mercury hallow cathode lamp of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded.

The cold vapour atomic absorption spectrophotometric method is suitable for all types of samples such as natural waters, potable waters, domestic and industrial wastewaters. Lower detection limit of 0·2 μg/l may be achieved.

5.2 Apparatus

5.2.1 *Atomic Absorption Spectrometer (AAS) and Associated Equipment*

Instrument settings recommended by the manufacturer shall be followed. Instruments designed specifically for the measurement of mercury using the cold vapour technique may be substituted for the AAS.

5.2.2 *Mercury Vapour Generation Assembly*

Consists of an absorption cell, peristaltic pump, flow meter, aeration tubing and a drying tube containing magnesium perchlorate.

5.2.3 *Mercury Hollow Cathode Lamp*

5.2.4 *Recorder / Printer / Display Meter*

Any multi-range variable recorder that is compatible with the UV detection system is suitable.

5.3 Reagents

5.3.1 *Sulphuric Acid* — Concentrated.

5.3.2 *Nitric Acid* — Concentrated.

5.3.3 *Stannous Chloride Solution*

Dissolve 25 g of stannous chloride ($SnCl_2$) in water containing 50 ml of concentrated hydrochloric acid and dilute to 250 ml. If a suspension forms, stir reagent continuously during use.

5.3.4 *Sodium Chloride* — Hydroxylamine sulphate solution.

Dissolve 12 g of sodium chloride and 12 g of hydroxylaminesulphate ($(NH_2OH)_2.H_2SO_4$ in distilled water and dilute to 100 ml.

5.3.5 *Potassium Permanganate Solution*

Dissolve 5 g of potassium permanganate in distilled water and dilute to 100 ml.

5.3.6 *Potassium Persulphate Solution*

Dissolve 5 g of potassium persulphate in distilled water and dilute to 100 ml.

5.3.7 *Stock Mercury Solution*

Dissolve 1·354 g of mercuric chloride in about 700 ml of distilled water. Add 10 ml of concentrated nitric acid and make up to 1 000 ml (1 ml = 1 mg Hg).

5.3.8 *Standard Mercury Solution*

Prepare a series of standard mercury solutions containing 0 to 5 µg/l by appropriate dilution of stock mercury solution (**5.3.7**) with water containing 10 ml of concentrated nitric acid per litre. Prepare standards daily.

NOTE — Use mercury free distilled water for the preparation of reagents and standards.

5.4 Procedure

5.4.1 *Instrument Operation*

Follow the procedure of the manufacturer's operating manual. Connect the mercury vapour generating assembly as shown in Fig. 1.

5.4.2 *Standardization*

Transfer 100 ml of each of the 1·0, 2·0 and 5·0 µg/l standard mercury solution and a blank of 100 ml water to 300 ml BOD bottles. Add 5 ml of concentrated sulphuric acid and 2·5 ml of concentrated nitric acid to each bottle. Add 15ml of potassium permanganate solution to each bottle and let stand for at least 15 minutes. Add 8 ml of potassium persulphate ($K_2S_2O_8$) solution to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulphate solution to reduce the excess permanganate. After decolourization add 5 ml of stannous chloride solution and attach the bottle immediately to the aeration apparatus forming a closed system. As mercury is volatilised and carried into the absorption cell, absorbance will increase to a maximum within a few seconds. As soon as recorder returns approximately to the base line, remove stopper holding the aeration frit from the reaction bottle and replace with a bottle containing distilled water. Flush the system for a few seconds and run the next standard in

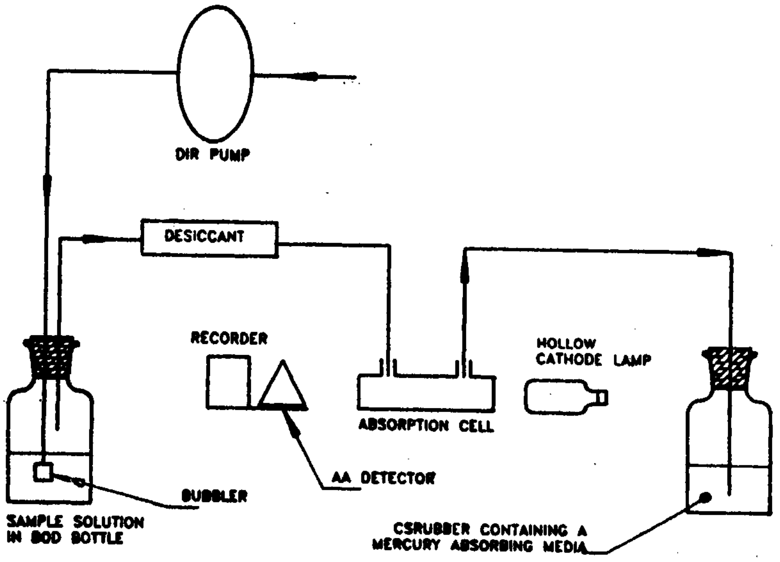

FIG. 1 SCHEMATIC ARRANGEMENT OF EQUIPMENT FOR MEASUREMENT OF MERCURY BY COLD VAPOUR ATOMIC ABSORPTION TECHNIQUE

the same manner. Construct a standard calibration curve by plotting absorbance (peak height) versus mercury concentration in μg.

5.4.3 *Analysis of Sample*

Transfer 100 ml of sample or portion diluted to 100 ml containing not more than 5·0 $\mu g/l$ mercury to a 300 ml BOD bottle. Treat as in **5.4.2** samples containing high (sea waters, brines and effluents high in chloride) chlorides require as much as an additional 25 ml potassium permanganate solution. During this step, chloride is converted into free chlorine which is absorbed at 253·7 nm. Hence remove all free chlorine before the mercury is reduced and swept into the cell by using an excess (25 ml) of hydroxylamine sulphate solution.

5.5 Calculation

Determine peak height of sample from recorder chart and read mercury value fron standard curve.

6 COLORIMETRIC DITHIZONE METHOD

6.1 Principle

Mercury ions react with dithizone solution in chloroform to form an orange colour which is measured at 490 nm using a spectrophotometer. The colorimetric dithizone method is suitable for estimating higher levels of mercury in potable waters (more than 2 $\mu g/l$) and has a minimum detection limit of 2 $\mu g/l$.

6.2 Interference

Copper, gold, palladium, divalent platinum and silver react with dithizone in acid solution. Copper in the dithizone extract remains in the organic phase while the mercury dissolves in the aqueous phase. The other contaminants usually are not present. The mercury dithizonate being photosensitive should be measured quickly.

6.3 Apparatus

6.3.1 *Spectrophotometer*

For use at 492 nm, providing a light path of 1 cm or longer.

6.3.2 *Separating Funnels*

250 and 1 000 ml with PTFE stopcocks.

6.3.3 *Glassware*

Clean all glassware with potassium dichromate-sulphuric acid cleaning solution.

6.4 Reagents

6.4.1 *Mercury Free Distilled Water*

Use redistilled or deionised distilled water for preparing all reagents and dilutions.

6.4.2 *Stock Mercury Solution*

Dissolve 135·4 mg of mercuric chloride ($HgCl_2$) in about 700 ml of distilled water, add 1·5 ml concentrated nitric acid and make up to 1 000 ml with distilled water (1·0 ml = 100 μg Hg).

6.4.3 *Standard Mercury Solution*

Dilute 10·0 ml of stock solution to 1 000 ml with distilled water. Prepare freshly before use (1·00 ml = 1·00 μg Hg).

6.4.4 *Potassium Permanganate Solution*

Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.4.5 *Potassium Persulphate Solution*

Dissolve 5 g of potassium persulphate ($K_2S_2O_8$) in 100 ml distilled water.

6.4.6 *Hydroxylamine Hydrochloride Solution*

Dissolve 50 g of hydroxylamine hydrochloride ($NH_2OH.HCl$) in 100 ml water.

6.4.7 *Dithizone Solution*

Dithizone is often contaminated with the oxidation product diphenyl thiocarbodizone or with metals. To purify dithizone dissolve 100 mg of dithizone in 50 ml of chloroform in a beaker and filter under slight vacuum using Whatman No. 42 or equivalent filter paper. Wash beaker and filter paper with 5 ml portions of chloroform. Transfer the filtrate to 500 ml separatory funnel. Add 100 ml of 1 percent minimum hydroxide and shake moderately for 1 minute only. Transfer chloroform layer to 250 ml separatory funnel retaining orange-red aqueous layer in a 500 ml funnel. Repeat extraction process keeping each time chloroform layers separately in 250 ml separatory funnels and using 1 percent a minimum hydroxide. After three extractions, transfer aqueous layer to 500 ml funnel. Discard chloroform layer.

Combine all the extracts in a 500 ml separatory funnel. Add 1 : 1 hydrochloric acid in 2 ml portions, mixing each time till dithizone precipitates and orange-red colour appears with three 25 ml portions chloroform. Dilute the combined extract to 1 000 ml with chloroform; 1 000 ml = 100 μg dithizone. Dilute 60 ml of this solution with chloroform to 1 000 ml, (1 ml = 6 μg dithizone).

6.4.8 *Sulphuric Acid* — 0·25 N.

Dilute 25 ml of 1 N sulphuric acid to 100 ml with distilled water.

6.4.9 *Potassium Bromide Solution*

Dissolve 40 g of potassium bromide in 100 ml distilled water.

6.4.10 *Chloroform*

6.4.11 *Phosphate-Carbonate Buffer Solution* — Dissolve 150 g of $Na_2HPO_4.12H_2O$ and 38 g of anhydrous potassium carbonate (K_2CO_3) in 1 litre of distilled water. Extract with 10 ml portions of dithizone until the last portion remains blue. Wash with chloroform to remove excess dithizone.

6.4.12 *Sodium Sulphate* — Anhydrous.

6.5 Procedure

6.5.1 *Preparation of Calibration Curve*

Pipette 0 (blank), 2·0, 4·0, 6·0, 8·0 and 10·0 ml of mercury standard solutions into separate beakers. To each beaker, add 500 ml of distilled water or that volume chosen for sample, 1 ml of potassium permanganate solution and 10 ml of concentrated sulphuric acid solution. Stir and boil if necessary, add more potassium permanganate until a pink colour persists. After boiling has ceased continuously add 5 ml of potassium persulphate ($K_2S_2O_8$) solution and let cool for 30 minutes. Add a few drops of hydroxylamine hydrochloride ($NH_2OH.HCl$) solution to discharge the pink colour. Cool and transfer each solution to individual 1 litre separating funnels. Add 25 ml of dithizone solution. Shake the separating funnel vigorously and transfer each organic layer to 250 ml separating funnel. Repeat this extraction atleast three times making sure that the colour in the last dithizone extract is an intense blue as that of the original dithizone solution. Wash accumulated dithizone extracts in the 250 ml separating funnel by shaking with 50 ml of 0·25 N sulphuric acid. Transfer washed dithizonate extract to another 250 ml separating funnel. Add 50 ml of 0·25 N sulphuric acid and 10 ml of potassium bromide solution and shake vigorously to transfer mercury dithizonate from organic layer to aqueous layer. Discard dithizone layer. Wash aqueous layer with a small volume of chloroform and discard the chloroform. Transfer 20 ml of phosphate carbonate buffer solution to each separating funnel and 10 ml standard dithizone solution. Shake vigorously and after separation, transfer the mercury dithizone to beakers. Dry contents with anhydrous sodium sulphate. Transfer mercury dithizonate solution to a cuvette and record absorbance at 492 nm. Plot absorbance versus mercury concentration in μg.

6.5.2 *Analysis of Samples*

Use 500 ml of sample and prepare an absorbance blank consisting of all reagents. When necessary, filter sample through glass wool into the separating funnel after oxidation step. Complete procedure as described in **6.5.1**.

6.6 Calculation

6.6.1 Read mercury from calibration curve.

6.6.2 After obtaining the above value, depending upon the volume chosen for analysis, calculate for 1 000 ml and report result in $\mu g/l$ Hg.

ANNEX A

(*Foreword*)

COMMITTEE COMPOSITION

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