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भारतीय मानक मसौदा

जल एवं अपशिष्ट जल के नमूने लेने और परीक्षण (भौतिक एवं रासायनिक) की पद्धतियाँ

भाग 48 पारा*(दूसरा पुनरीक्षण)**Draft Indian Standard***Methods of Sampling and Test (Physical And Chemical) for Water and Wastewater****Part 48 Mercury***(Second Revision of IS 3025 (Part 48))*

ICS 13.060.50

Water Quality Sectional Committee, CHD 36**Last Date of Comment:****27 December 2024****FOREWORD**

(Formal clause to be added later)

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.

The Technical Committee responsible for formulation of IS 2488 (Part 2): 1968 'Methods of Sampling and Test for Industrial Effluents, Part II' and IS 3025: 1964 'Methods of sampling and test (physical and chemical) for water used in industry' decided to revise the standard and publish it in separate parts. This method superseded 13 of IS 2488 (Part 2): 1968 'Methods of sampling and test for industrial effluents, Part 2, and was one among the different parts published under IS 3025 series of standards. The first revision of this standard was published in 1994.

In this second revision the following changes have been incorporated:

a) The colorimetric dithizone method has been deleted as it is a manual method and has become obsolete. Additionally, since drinking water limits are at the parts per billion (ppb) level, this method encounters errors during determination; and

b) Inductively coupled plasma spectroscopy methods have been incorporated.

In the preparation of this standard, considerable assistance has been derived from standard methods for the examination of water and wastewater published by American Public Health Association, Washington. USA, 24th edition, 2024.

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: 2022 ‘Rules for rounding off numerical values (*second revision*)’.

1 SCOPE

This standard (Part 48) prescribes the following two methods for the determination of mercury in water and wastewater:

- a) Cold Vapour Atomic Absorption Spectrophotometry method; and
- b) Inductively Coupled Plasma Mass Spectrometry.

2 REFERENCES

The Indian Standards given below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions, indicated were valid. All standards are subject to revisions and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of these standards:

<i>IS No.</i>	<i>Title</i>
IS 3025	Methods of sampling and test (physical and chemical) for water and wastewater
(Part 64) : 2015	Part 64 Application of Inductively Coupled Plasma Mass Spectrometry (ICP - MS) - General Guidelines
(Part 65) : 2022	Part 65 Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) — Determination of selected elements including Uranium Isotopes (first revision)
IS 7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents, Part 1
IS 7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents, Part 2
IS 17614	Water Quality — Sampling
(Part 1) : 2021	Part 1 Guidance on the design of sampling programmes and sampling techniques
(Part 3) : 2021	Part 3 Preservation and handling of water samples

3 TERMINOLOGY

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

4 SAMPLE PRESERVATION

The sampling and storage shall be done as prescribed in IS 17614 (Part 1) and IS 17614 (Part 3). Additionally, 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. Glass storage containers are preferred to plastic, to extend holding time to 30 days, rather than only 14 days allowed in plastic containers. For preservation, the sample should be acidified with concentrated nitric acid (2 ml of AR grade nitric acid in 1 l of the sample just to bring down the pH below 2). For dissolved mercury, filter the sample in the field and acidify the filtrate with nitric acid to a pH 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

5.1.1 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 hollow cathode lamp of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded.

5.1.2 The cold vapour atomic absorption spectrophotometric method is suitable for all types of samples such as natural waters, potable waters, domestic and industrial wastewaters.

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, are available commercially and may be substituted for the AAS. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at specified concentrations.

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 I Printer I 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 (H_2SO_4), Concentrated.

5.3.2 Nitric Acid (HNO_3), Concentrated.

5.3.3 Stannous Chloride ($SnCl_2$) Solution

Dissolve 25 g of analytical grade 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 ($(NH_2OH)_2.H_2SO_4$) Solution.

Dissolve 12g of sodium chloride and 12 g of hydroxylamine sulphate ($(NH_2OH)_2.H_2SO_4$) in distilled water and dilute to 100 ml. A 10 percent hydroxylamine hydrochloride ($NH_2OH.HCl$) solution may be substituted for the hydroxylamine sulphate.

5.3.5 Potassium Permanganate ($KMnO_4$) Solution

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

5.3.6 Potassium Persulphate ($K_2S_2O_8$) 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 $\mu g/l$ 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 $\mu\text{g}/\text{l}$ standard mercury solution and a blank of 100 ml mercury free distilled water to BOD bottle or 250 ml Erlenmeyer flasks with ground glass joint. Add 5 ml of concentrated sulphuric acid and 2.5 ml of concentrated nitric acid to each bottle. Add 15 ml of potassium permanganate (KMnO_4) solution to each bottle and let stand for at least 15 min. Add 8 ml of potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) solution to each bottle and heat for 2 h in a water bath at 90 °C to 95 °C. Cool to ambient temperature. To each BOD bottle or flask, add sodium chloride - hydroxylamine solution to reduce the excess permanganate. After decolorization, add 5 ml of stannous chloride solution and immediately attach the bottle to the aeration apparatus forming a closed system. As mercury is volatilized 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 the same manner. Construct a standard calibration curve by plotting absorbance (peak height) versus mercury concentration in μg .

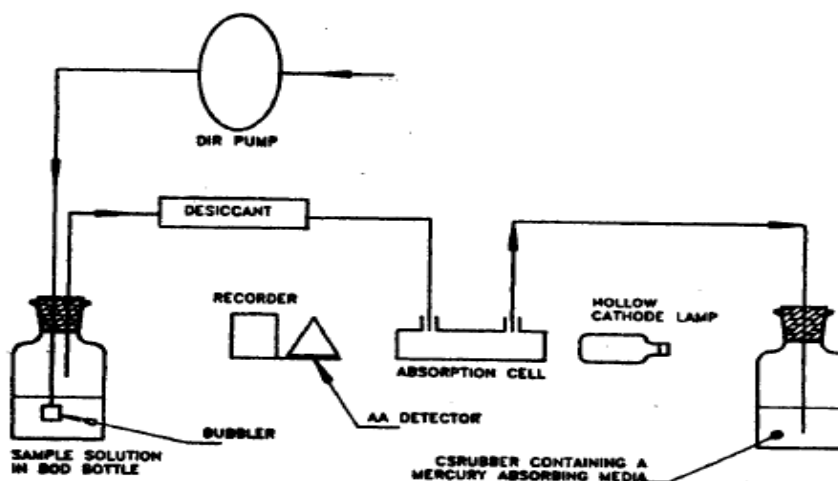


FIG. 1. SCHEMATIC ARRANGEMENT OF EQUIPMENT FOR MEASUREMENT OF MERCURY BY COLD VAPOUR ATOMIC ABSORPTION TECHNIQUE

5.4.3 Analysis of Sample

Transfer 100 ml of sample or portion diluted to 100 ml containing not more than 5.0 $\mu\text{g/l}$ mercury to a BOD bottle. Treat as given in 5.4.2. Samples containing high chlorides (sea waters, brines and effluents high in chloride) 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 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 from standard curve.

6 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Mercury can also be determined by inductively coupled plasma mass spectroscopy with reference to procedure given in IS 3025 (Part 64) and IS 3025 (Part 65) determination of mercury in water and wastewater.