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भारतीय मानक मसौदा

वायु प्रदूषण मापने की विधियाँ

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अनुभाग 1 समामेलन सिद्धांत द्वारा शीत-वाष्प परमाणु प्रतिदीप्ति स्पेक्ट्रोमीटर विधि

Draft Indian Standard

METHODS FOR MEASUREMENT OF AIR POLLUTION

Part 29 Vapor Phase Mercury in Ambient Air

Section 1 Cold-Vapor Atomic Fluorescence Spectrometer

Method by Amalgamation Principle

ICS 13.040.20

Air Quality Sectional Committee, CHD 35

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FOREWORD

(Formal clause will be added later)

Mercury is a persistent toxic contaminant in the environment. It is an important air pollutant because of its detrimental health effects. Coal-burning power plants, chlor-alkali industry, crematoria, coal tar uses, damaged mercury products, burning and disposal of wastes containing mercury are the major sources of mercury emissions into air. Mercury in ambient air occur mostly in the elemental vapor form except at certain coastal and industrial locations.

Mercury is a potent neurotoxin, and chronic exposure, particularly through the inhalation of vapor phase mercury, can pose serious health risks. Beyond human health concerns, mercury also affects ecosystems as it accumulates in water bodies, leading to methylmercury formation, a highly toxic form of mercury that bio accumulates in aquatic organisms. Monitoring vapor phase mercury is, therefore, critical for protecting human health and the environment.

Measurement of vapor phase mercury in ambient air is achieved through specialized analytical techniques such as Cold Vapor Atomic Absorption Spectrometry (CVAAS) or Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). These methods allow for the quantification of mercury concentrations in air samples and help researchers and environmental agencies track variations in mercury levels over time and across different geographical locations.

This Indian Standard is published in several parts. The other parts in this series are:

Part 1 dust fall (First Revision)

Part 2 Sulphur Dioxide

Sec 1 Tetrachloromercurate Pararosaniline method

Sec 2 ultraviolet fluorescence method

Part 3 Radioactivity (particulate in air)

Part 4 suspended Particulate matter (First Revision)

Part 5 Sampling of Gaseous Pollutants (*First Revision*)

Part 6 oxides of nitrogen (*First Revision*)

Sec 2 chemiluminescence method

Part 7 Hydrogen Sulphide (*First Revision*)

Part 8 sulphation rate

Part 9 oxidants

Part 10 carbon monoxide (*First Revision*)

Part 11 benzene, toluene and xylene (BTX) (*Second Revision*)

Part 12 polynuclear aromatic hydrocarbons (PAHs) in air particulate matter (*First Revision*)

Part 13 total fluorides in ambient air

Part 14 guidelines for planning the sampling of atmosphere (*Second Revision*)

Part 15 mass concentration of particulate matter in the atmosphere

Sec 2 Beta-ray absorption method

Part 16 recommended practice for collection by filtration and determination of mass, number and optical sizing of atmospheric particulates

Part 17 C1 to C2 hydrocarbons in air by gas chromatography

Part 18 continuous analysis and automatic recording of the oxidant content of the atmosphere

Part 19 Chlorine (*first revision*)

Part 20 carbon disulphide

Part 21 non methane hydrocarbons in air by gas chromatography

Part 22 lead

Part 23 respirable suspended particulate matter (PM 10), cyclonic flow technique

Part 24 Fine Particulate Matter (PM 2.5)

Part 25 ammonia

Part 26 Nickel

Part 27 Vapour-Phase Organic Chemicals Vinyl Chloride to nC22 Hydrocarbons in air and Gaseous Emissions by Diffusive (Passive) Sampling onto Sorbent Tubes or Cartridges Followed by Thermal Desorption (TD) and Capillary gas Chromatography (GC) Analysis.

Part 28 Vapour-Phase Organic Chemicals C3 to nC30 Hydrocarbons in Air and Gaseous Emissions – Sampling by Pumped Sorbent Tubes Followed by Thermal Desorption (TD) and Capillary gas Chromatography (GC) Analysis.

Part 29 Vapor Phase Mercury in Ambient Air

Sec 2 Cold-Vapor Atomic Absorption or Fluorescence Spectroscopy (CVAFS) Method Using Acidified solution of KMnO₄

Part 30 Metals in Particulate Matter in Ambient Air

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: 2022 'Rules for rounding off numerical values (*second revision*)

Draft Indian Standard
Methods for Measurement of Air Pollution
Part 29 Vapor Phase Mercury in Ambient Air

Section 1 Cold-vapor atomic fluorescence spectrometer method by amalgamation principle

1 SCOPE

This standard prescribes the amalgamation principle for the measurement of concentration of Vapor Phase Mercury (Hg) present in the ambient air using cold-vapor atomic fluorescence spectrometer (CVAFS).

2 REFERENCE

The standards listed 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 revision, and parties to agreements based on these standards are encouraged to investigate the possibility of applying the most recent editions of the standards listed below:

<i>IS No.</i>	<i>Title</i>
IS 4167 : 2020	<i>Glossary of terms relating to air pollution (second revision)</i>

3 TERMINOLOGY

For this standard, the definitions given in IS 4167 shall apply.

4 PRINCIPLE

The collection of mercury from ambient air is based on the amalgamation principle and takes advantage of the property of mercury to form gold-mercury amalgam on the surface of gold-coated substrate (particles/wires/beads). The mercury vapor from the ambient air is collected by drawing air through an adsorbent tube containing gold coated on a suitable substrate using a low flow rate (0.3 Lpm to 0.5 Lpm). The mercury in air gets adsorbed and forms an amalgam on the surface of gold coated substrate. The amount of vapor-phase mercury collected on a gold-coated substrate adsorbent tube is determined using cold-vapor atomic fluorescence spectrometer (CVAFS). The sample adsorbent tube is heated to release the collected mercury. The desorbed mercury is carried in an inert gas stream (He or Ar) to a second adsorbent tube containing gold-coated substrate (the analytical adsorbent tube). The mercury collected on the analytical adsorbent tube is then thermally desorbed and carried into the CVAFS analyzer. The resulting voltage peak is integrated to produce peak area for the sample.

5 DETECTION LIMIT

The detection limits achieved using this method is 45 ng/m³ for vapor-phase mercury.

6 INTERFERENCES

Interferences may occur during sampling stage where the sulfur species, organic compounds and water vapor may co-adsorb on adsorption tubes. However, these interfering species are desorbed completely during the analysis procedure, they may affect the adsorption efficiency of mercury on the adsorbent.

7 REQUIREMENTS

7.1 For Preparation of Gold-Coated Bead Adsorbent Tubes

Sputter coater with 24 karat gold source, borosilicate glass beads (1 mm diameter), quartz tubes (10 cm length, 7 mm O.D., 5 mm I.D.), quartz wool, Teflon end plugs, rigid plastic tubes with endcaps for gold adsorbent tube storage, Teflon tape (½”), Polyethylene tube bags and heat sealer.

7.2 For Preparation of Glass Fiber Filters

Glass fiber filters (47 mm), ceramic crucible.

7.3 For Sample Collection

Teflon filter holders (47 mm), tweezers, particle-free gloves, resealable polyethylene bags, Teflon tape (1” and ½”), Teflon tubing (¼” O.D.), polyethylene tubing (3/8” O.D.)

7.4 For Sample Analysis

CVAFS system, carrier gas (argon or helium ultra-high purity (99.999 percent), purge gas (nitrogen, pre-purified (99.998 percent), gas tight syringe (100 µL), injection port, valve and septa for injection port, elemental mercury (liquid, high purity), constant temperature (± 0.1°C) circulating water bath, certified immersion thermometer.

7.5 Preparation of Gold-Coated Beads and Adsorbent Tube

Borosilicate glass beads (1 mm diameter) are coated with a gold plasma generated under vacuum using a sputter coater. The thickness of the gold coating produced should be approximately 300 Angstrom. All components of the adsorbent tubes are heated in a muffle furnace to remove any Hg prior to assembling adsorbent tubes. The gold-coated beads are baked at 500 °C for one hour, the quartz wool at 600°C for one hour, and the quartz tubes at 700 °C for one hour.

a) Construction of Adsorbent Tube

A small amount of quartz wool is rolled into a ball and placed in the quartz tube forming a short (0.25 cm) plug. About 0.7 g of the gold-coated beads are added to the quartz tube on top of the quartz wool. A second ball of quartz wool is placed in the quartz tube so that it rests on top of the beads. Tubes should be packed as tightly as possible without breaking the quartz wool fibers.

b) Adsorbent Tube Conditioning and Testing

New adsorbent tubes are conditioned prior to use by drawing air through the adsorbent tube at 0.3 Lpm for 30 minutes and then blanked by heating the adsorbent tube to 500°C for five minutes while an inert gas (i.e., He) flows through the adsorbent tube at 0.3 Lpm. The conditioning procedure is performed twice prior to testing the adsorbent tube. New adsorbent tubes are evaluated for their reproducibility in collecting vapor-phase Hg and for their blank levels prior to use.

Adsorbent tubes to be used in vapor-phase Hg sample collection are prepared by blanking them, Teflon-taping the end plugs to the adsorbent tubes, placing the adsorbent tubes in the plastic storage tube, sealing the tube in polyethylene, and then placing two gold adsorbent tubes for a sample in a resealable polyethylene bag.

8 SAMPLING

8.1 Sampling Equipment

The pumps used for collection of mercury samples in ambient air should be capable of trace-level pollutant sampling. High efficiency, oil less, brushless pumps should be used and protected from weather (i.e., the pump housing should be well sealed from rain, insulated and heated during the winter, and fan cooled during the summer).

A fiberglass enclosure is used as the sample box to house the adsorbent tubes during sample collection. The box is mounted on a pole or tower at least 3 meters above ground level. The pump is connected to the sample box using the polyethylene tubing with quick connect couplings.

Moisture on gold surface interferes with the amalgamation of Hg. Therefore, condensation during collection of vapor-phase Hg must be prevented. To prevent condensation in the gold adsorbent tubes during sampling, a heat tube is used to keep the temperature of the adsorbent tubes above ambient temperature. The heat tube is constructed from heat tape wrapped around a metal tube, insulated and covered with heat-shrink electrical tubing and electrical tape.

8.2 Collection of Samples

Pre-baked (at 400°C) glass fiber filter is loaded in the filter cassette and placed in the sample box. The gold adsorbent tubes are taken from their plastic storage tubes and the end plugs are removed. Vapor phase Hg samples are collected using two gold adsorbent tubes in series as a quality control measure. The 'A' adsorbent tube is connected to the Teflon tubing from the outlet of the filter cassette. A short piece of Teflon tubing is placed in the outlet of the 'A' adsorbent tube. The 'B' adsorbent tube is then attached to the Teflon tubing. The heat tube assembly is positioned to cover the 'A' adsorbent tube. To begin the sample, the Teflon tubing at the pump's end is attached to the outlet of the 'B' adsorption tube. Record the following parameters: date, sampling location, time, ambient temperature, barometric pressure, relative humidity, rotameter reading, and gold adsorbent tube number. Allow the sampler to operate for the desired time. The pump is turned off and the glass fiber prefilter is discarded or can be stored for other uses at the end of the sampling period, record the parameters again listed above. If the sampling time is more than 1 hour, record these parameters every hour. If the flows at the beginning and end of the sampling period differ by more than 10 percent, mark the adsorbent tube as suspect.

Calculate and record the average sampling flow rate for the adsorbent tube according to the following equation:

$$Q_a = \frac{Q_1 + Q_2 \dots \dots + Q_N}{N}$$

where,

Q_a = Average flow rate in Lpm.

Q_1, Q_N = Flow rates determined at the beginning and end points during sampling.

N = Number of points averages.

Calculate and record the total volumetric flow for the adsorbent tube using the following equation:

$$V_m = \frac{TXQ_a}{1\ 000}$$

where,

V_m is Total volume sampled (m³) at measured temperature and pressure

T is Sampling time (minutes)

1000 is for Conversion of litre to m³

The total volume (V_s) at standard conditions, 25°C and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where,

V_s is Total sample volume (m³) at standard conditions, 25° C and 760 mmHg.

P_A is Average barometric pressure, mmHg.

t_A is Average ambient temperature, °C

The adsorbent tubes are removed from the sampling box and the end plugs are replaced. The end plugs are sealed to the adsorbent tubes with Teflon tape and the adsorbent tubes are returned to their respective plastic tubes and capped. Labels with unique sample identification numbers are affixed to each tube. The tubes are sealed in polyethylene bags and returned to the laboratory for analysis. The Teflon tubing connector should be returned to the laboratory for cleaning. The samples can be stored up to one week at 4°C until analyzed.

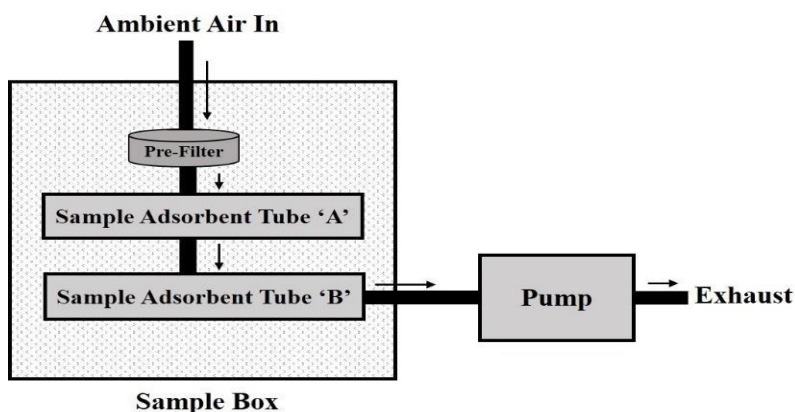


FIG 1: BLOCK DIAGRAM OF THE SAMPLING SYSTEM

9 ANALYSIS

9.1 The Analytical System

9.1.1 The analytical system consists of a pair of adsorbent tubes in series, a thermal desorption system, a CVAFS mercury detector, an integrator to convert peak voltage to peak area, and an inert carrier gas (He or Ar).

9.1.2 The dual-amalgamation technique requires two gold adsorbent tubes in series: a 'sample' adsorbent tube and an 'analytical' adsorbent tube. This technique has two main advantages: it virtually eliminates interferences due to organics and Cl₂ from the sample adsorbent tube and provides greater analytical precision because the same analytical adsorbent tube is being used to introduce the Hg into the detector for all the samples.

9.1.3 The thermal desorption system includes a pair of nickel-chromium coils each with a variable transformer to regulate the output, a pair of small axial fans to cool the coils and adsorbent tubes quickly, and a programmable circuit controller to coordinate the adsorbent tube heating and cooling cycles.

9.1.4 Power supplied to the CVAFS should be stabilized by a power conditioner to reduce line voltage fluctuations. The instrument is left on continuously to stabilize the UV lamp and maintain consistency from one day to the next.

9.1.5 The carrier gas should be mass-flow controlled to produce a more consistent peak response. Ultrahigh purity gas should be used, and an adsorbent tube (conditioned and tested) called pre-adsorbent tube be placed upstream of the sample and analytical

adsorbent tubes to remove any remaining traces of Hg in the gas.

9.1.6 The vapor phase Hg analytical system requires an injection port and gas-tight syringe (100 μ L) to introduce Hg standards into the sample train.

9.1.7 An injection port with valve and Teflon-coated septum are used for injecting Hg saturated air onto gold adsorbent tubes in the analytical system. The port is placed after pre-adsorbent tube in line for the calibration process and then removed.

9.2 Generation of Hg Standard Vapor

A small amount (2-3 mL) of liquid metallic Hg is placed in a closed 150 mL flask to generate Hg saturated air above the liquid surface. The flask is immersed in a constant temperature ($\pm 0.1^\circ\text{C}$) circulating water bath. A certified immersion thermometer should be used to monitor the temperature of the air above the mercury in the flask. The temperature of the air in the flask must be maintained below room temperature otherwise, the Hg will condense on the walls of the injection apparatus.

The gas-tight 100 μ L syringe should rest on top of the flask with the needle portion protruding through a valve into the flask air. Hg saturated air from the flask should be drawn up into the syringe and allowed to equilibrate.

Alternatively, the mass of the mercury contained per unit volume of mercury-saturated air at a given temperature can be calculated using the following empirical equation known as Dumarey equation.

$$\gamma_{\text{Hg}} = \frac{D}{T} 10^{-A + [B + T]}$$

where,

γ_{Hg} is the mass concentration of saturated mercury in the air inside the calibration vessel, in ng/ml,

T is the temperature of the air inside the calibration vessel in Kelvin (K),

A is a constant equal to -8.134 459 741,

B is a constant equal to 3 240.871 534 K,

D is a constant equal to 3 216 522.61 K ng/ml.

9.3 Injection System Calibration

The injection system is conditioned before each day of analysis to ensure precise and reproducible results. The process includes the following steps: (i) condition the syringe by flushing it three times with Hg saturated air, filling it to capacity, and allowing it to equilibrate for 15 minutes, (ii) place a new septum in the injection port and condition them both with multiple injections of Hg saturated air before initiating calibration.

The flask should be periodically flushed (approx. once per month) with pre-filtered N_2 gas in order to displace any oxygen which may oxidize the surface of the liquid mercury and prevent volatilization. Also, the valve for the syringe on the flask should be above the level of the water in the water bath. If water gets into the flask, it should be purged with N_2 gas.

9.4 Calibration of CVAFS Instrument

A calibration curve, generated by injection of different known volumes of Hg saturated air onto a gold adsorbent tube, must be performed before each analysis. The amounts of Hg injected for the calibration curve should be adjusted to the expected value of the samples to be analyzed. The calibration curve should cover a range of $\pm 5\%$ of the expected value of the samples. To generate standard injections for the calibration curve, the conditioned injection port is placed in the analytical train in front of the gold adsorbent tube to be used for generating the standard curve (called the "standard adsorbent tube"). A specified volume of Hg saturated air is withdrawn from the flask using the gas tight syringe and injected onto the blanked standard adsorbent tube through the injection port valve. After the injection the syringe is returned to the flask and filled to capacity until the next injection. The temperature of the air in the flask is recorded for each injection to calculate the actual amount of Hg injected.

A calibration curve is performed beginning with a zero point (0 μ L) and continuing in ascending order to the highest amount. The zero point of the calibration curve is generated in the same manner described above except that no Hg saturated air is injected into the port. The amount of Hg emitted from the needle tip and the injection apparatus and adsorbed onto the gold adsorbent tube is called the zero point (typically between 1-5 pg Hg).

9.4 Sample Analysis

After a satisfactory calibration curve for the CVAFS is obtained, sample adsorbent tubes are analyzed by dual amalgamation CVAFS. The analytical procedure for detection of mercury using CVAFS includes three main steps. First, the sample adsorbent tube is placed in the analytical system and heated to release the collected mercury. The released mercury is entrained by the gas stream, carried into the analytical adsorbent tube where it is amalgamated to the gold surface. Second, the analytical adsorbent tube is heated to release the mercury which then carries into the CVAFS detector cell. Third, the mercury in the detector cell absorbs UV light and the resulting fluorescence is converted to a voltage proportional to the amount of Hg detected by a photomultiplier tube. An integrator then converts the voltage response to peak area.

Control standards should be analyzed at regular intervals during the analysis of samples to detect any drift in the response or change in sensitivity of the CVAFS instrument. Control standards are generated in the same manner as the calibration standards. The volume of Hg saturated air injected for a control standard should be representative of the Hg concentration of the samples being analyzed.

The predicted value of the control standards should be within 5 percent of the calibration curve before continuing to analyze samples. If subsequent control standards also deviate by more than 5 percent from the calibration curve, it is likely that the analyzer sensitivity has changed and a second calibration curve should be generated.

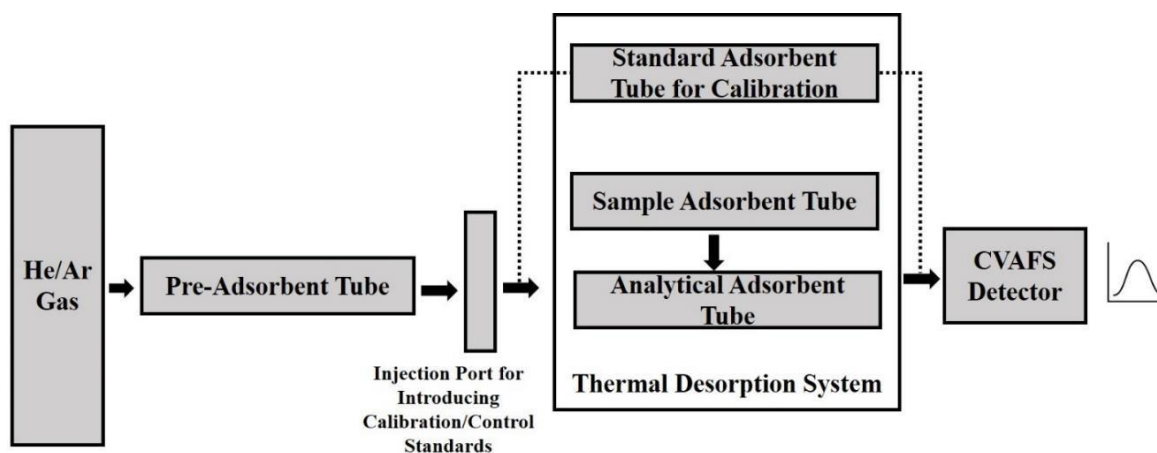


FIG 2: BLOCK DIAGRAM OF THE ANALYTICAL SYSTEM

10 CALCULATIONS

10.1 Calculation of mercury concentrations in ambient air

Vapor phase mercury concentrations in ambient air are reported in ng/m³. The amount of mercury collected on a gold-coated bead sample adsorbent tube (ng Hg) is calculated from the integrator response for the sample [in Peak Area Units (PAU)] multiplied by the slope of the calibration curve, which is in ng Hg/PAU. The amount of mercury collected on a gold-coated bead sample adsorbent tube is blank corrected by subtracting the average amount of mercury collected on field blank adsorbent tube.

As mentioned above the vapor phase mercury samples are typically collected using 2 gold-coated bead sample adsorbent tubes in series (the exit from the first adsorbent tube is connected to the inlet of the second adsorbent tube). The total amount of Hg collected for the sample is then calculated by simple addition of the blank corrected amounts of mercury from the two sample adsorbent tubes.

The volume (m³) of air sampled is calculated by multiplying the flow rate through the sample adsorbent tubes (in Lpm) by the duration of the sample (min) and converting the product from L to m³. The ambient vapor phase mercury concentration in ng Hg/m³ is calculated from the total blank corrected ng of Hg for the sample adsorbent tubes divided by the cubic meters of air sampled.

$$\text{Volume of Air Sampled (m}^3\text{)} = \frac{\text{Flow Rate (Lpm)}}{1\,000} \times \text{Duration (min)}$$

$$\text{Amount of Hg (ng)} = \text{Integrator Response (PAU)} \times \text{Slope of Calibration Curve (ng/PAU)}$$

$$\text{Total Amount of Hg for sample (ng)} = (\text{Sample} - \text{Average Field Blank})$$

$$\text{Concentration (ng / m}^3\text{)} = \frac{\text{Total Amount of Hg for Sample (ng)}}{\text{Standard Volume of Air Sampled (m}^3\text{)}}$$