CHD 35 (25502) WC
September 2024

BUREAU OF INDIAN STANDARDS

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भारतीय मानक मसौदा

वायु प्रदूषण मापने की विधियाँ

भाग 29 परिवेशी वायु में वाष्प चरण पारा

अनुभाग 2 शीत-वाष्प परमाणु अवशोषण या $KMnO_4$ के अम्लीय घोल के उपयोग द्वारा प्रतिदीप्ति स्पेक्ट्रोस्कोपी (CVAFS) विधि

Draft Indian Standard

METHOD MEASUREMENT OF AIR POLLUTION

Part 29 Vapor Phase Mercury in Ambient Air

Section 2 Cold-Vapor Atomic Absorption or Fluorescence Spectroscopy (CVAFS) Method Using Acidified solution of $KMnO_4$

ICS 13.040.20

Air Quality Sectional Committee, CHD 35

Last Date for Comments: 11th November 2024

Air Quality Sectional Committee, CHD 35

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 methyl mercury 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 maiter (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 1 Cold-Vapor Atomic Fluorescence Spectrometer method by Amalgamation Principle

Part 30 Metals in Particulate Matter in Ambient Air (under WC)

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).*

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Draft Indian Standard

Method Measurement of air pollution

Part 29 Vapor Phase Mercury in Ambient Air

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

1 SCOPE

This standard prescribes the acidified solution of $KMnO_4$ principle for the measurement of concentration of vapor Phase mercury (Hg) present in the ambient air using cold-vapor atomic fluorescence spectrometer (CVAFS).

2 REFERENCES

The Indian 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 this Indian standard are encouraged to investigate the possibility of applying the most recent editions of these standards.

IS No.	***Title***
4167 : 2020	Glossary of Terms Relating to Air Pollution (*Second Revision*)

3 TERMINOLOGY

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

4 PRINCIPLE

The elemental mercury in ambient air is collected in acidified solution of $KMnO_4$ in a series of impingers placed in an ice bath. Samples are analyzed for mercury using cold-vapor atomic absorption (CVAAS) or fluorescence spectroscopy (CVAFS). CVAAS method is 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 an atomic absorption spectrometer. Absorbency is measured as a function of mercury concentration.

5 DETECTION LIMIT

The detection limit achieved using this method is 0.5 $\mu g/m^3$.

6 INTERFERENCES

Interferences may occur where the sulphur species are present in the atmosphere in large quantities (in ppm range).

7 APPARATUS

7.1 A water bath for sample digestion

7.2 Ice Bath

7.3 Quartz fiber filter (47 mm)

7.4 filter holder (47 mm)

7.5 A CVAAS or CVAFS system

8 REQUIREMENTS

8.1 For sample collection

Sampling train containing two or more impingers (according to the expected concentration of Hg present in the sampling location's ambient air), 47 mm quartz fiber filter, filter holder (47 mm), silica gel dryer and a pump. Tweezers and particle free gloves required for sample handling

8.2 Reagents

8.2.1 *Hydroxylamine Sulfate ($NH_2OH.H_2SO_4$)* — solid

8.2.2 *Stannous chloride ($SnCl_2.H_2O$)* — solid

8.2.3 *Mercury Standard Solution* — a certified (1000 µg/ml) mercury standard

8.2.4 *H_2SO_4-$KMnO_4$ Absorbing Solution (4 percent w/v $KMnO_4$, 10 percent v/v H_2SO_4)*

a) 4 percent w/v $KMnO_4$ — Dissolve 40 g $KMnO_4$ in 10 percent v/v H_2SO_4 and make up the volume to 1 Lwith 10 percent v/v H_2SO_4 .

b) percent v/v H_2SO_4 — Mix carefully with stirring 100 ml of concentrated H_2SO_4 into approximately 800 ml of water following the standard acid to water mixing procedure and make up the volume to 1 L with water.

NOTE — H 2SO4 –KmnO4 absorbing solution must be prepared fresh prior to sampling.

8.2.5 *Stannous chloride solution*

Dissolve 100 g in 10 percent v/v HCl and dilute with 10 percent v/v HCl to 1 L. Difficulty in dissolving the stannous chloride can be overcome by dissolving in a more concentrated HCl solution (such as 100 ml of 50 percent v/v HCl) and diluting to 1 L with water**.**

8.2.6 *Mercury standards*

a) 10 mg/L Hg stock solution — Dilute 1 ml of 1000 mg/L Hg standard solution to 100 ml with 10 percent v/v HCl

b) 100 µg/L Hg Stock solution—Dilute 1ml of 10 mg/L Hg stock solution to 100 ml with 10 percent v/v HCl.

c) Working Hg standards—Prepare working standards of 1, 5, 10, and 20 µg/L Hg from the 100 µg/L Hg Stock solution by diluting 1 ml,5 ml ,10 ml and 20 ml each to 100ml with 10 percent v/v HCl. If samples to be analyzed contains less than 1 µg/L Hg, working standards should be prepared at 0.05, 0.1, 0.5, and 1 µg/L Hg from 10 µg/L Hg standard solution.

Caution: Pressure may build up in the solution storage bottle because of a potential reaction between potassium permanganate and acid. Therefore, these bottles should not be fully filled and should be vented to relieve excess pressure. Venting should be in a manner that will avoid any contamination of the solution.

9 SAMPLING:

9.1 Sampling Train:

Place 30 ml (or up to 3cm depth of impinger) H_2SO_4 $KMnO_4$ absorbing solution in two consecutive impingers connected in series (the number of impingers can be increased if a higher concentration of Hg is expected). The impingers are preceded with a pre-baked (at 400 °C) 47 mm filter to trap the dust particles and succeeded with silica gel dryer, rotameter and pump. The impingers should be placed in an ice bath to maintain a constant temperature of (20 °C to 25 °C).

9.2 Sampling Procedure:

Assemble the sampling train and start the pump. Let it run for the desired duration. Record the flow rate before and after sampling. The pump is turned off after completion of sampling and the glass fiber filter is discarded or can be stored for other uses. The impingers are sealed immediately after the sampling ends and are transported to the laboratory for analysis. Calculate the average sampling flow rate, total volumetric flow and total volumetric flow at standard conditions as per the Eq. 1, 2 and 3, respectively mentioned in Method 1. Similarly, a filed blank is also collected where the sampling train is set but the pump is not switched on. Field blank collection is essential so as to ensure that there is no contamination due to sampling activities

10 ANALYSIS

10.1 CVAAS/CVAFS calibration

The calibration of the CVAAS/CVAFS instrument is performed according to the manufacture's guidelines. To produce the cold vapors of mercury, stannous chloride solution is added to reduce the oxidized mercury to its elemental sate. The mercury-laden solution is then purged with the carrier gas i.e Argon (Ar) or Nitrogen(N_2) into the atomic absorption cell. This procedure is used to calibrate the instrument using 10% v/v HCl as the blank along with standards described in section **4.2.6**. Alternatively, the standard mercury vapors can also be produced using the method described in section **8.2** of Method 1.

10.2 Sample Analysis

The collected samples are analyzed by CVAAS. The sample should be prepared immediately prior to analysis. Dissolve by incrementally adding approximately 500 mg 0f solid hydroxylamine sulfate into the sample until a clear, colorless solution persists to reduce the excess permanganate. Add the hydroxylamine slowly because of the violence of the reaction. Add stannous chloride to the sample solution (if such provision is already not available in the instrument) and immediately attach the sample container to aeration apparatus of the instrument and purged in to the atomic absorption cell with the carrier gas i.e Argon (Ar) or Nitrogen(N_2) and the instrument reading is recorded.

11 CALCULATION

The volume (m^3) of air sampled is calculated by multiplying the flow rate through the impingers (in Lpm) by the duration of the sample (min) and converting the product from L to m^3. The ambient vapor phase mercury concentration in µg Hg/m^3 is calculated from the total blank corrected µg of Hg for the sample divided by the cubic meters of air sampled.

$$\text{Volume of Air Sampled } (m^3) = \frac{\text{Flow Rate (Lpm)}}{1000} \text{ x Duration (min)}$$

$$\text{Amount of Hg (µg) = Absorbance (Abs) x Slope of Calibration Curve (µg/Abs)}$$

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

$$\text{Concentration } (\mu g/\, m^3) = \frac{Total\ Amount\ of\ Hg\ for\ sample\ (\mu g)}{Standard\ Volume\ of\ Air\ Sampled\ (m^3)}$$