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Indian Standard
**METHODS OF
MEASUREMENT OF AIR POLLUTION**

PART 13 TOTAL FLUORIDES IN AMBIENT AIR

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**BUREAU OF INDIAN STANDARDS
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FOREWORD

This Indian Standard (Part 13) 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.

Fluoride may be found in the air as gas or as particulate matter being introduced through industrial emissions containing fluoride compounds in both states. The industries which utilize fluoride containing compounds or emit fluorides as a result of manufacturing processes include those concerned with mining and processing of phosphate rock and other fluoride containing minerals and production of fertilizers, aluminium, steel, glass and various other chemical products.

The presence of excessive concentration of fluoride compounds in atmosphere can be damaging to all forms of life. Excessive quantities of fluorides in man results in bone and teeth abnormalities and also causes fluorosis.

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 MEASUREMENT OF AIR POLLUTION

PART 13 TOTAL FLUORIDES IN AMBIENT AIR

1 SCOPE

1.1 This standard prescribes two methods for the determination of total fluorides in ambient air:

- a) Zirconium SPADNS method, and
- b) Selective ion electrode method.

1.2 In case of dispute selective ion electrode method shall be the referee method.

2 REFERENCES

2.1 The following Indian Standard is a necessary adjunct to this standard:

IS No.	Title
IS 4167 : 1980	Glossary of terms relating to air pollution (<i>first revision</i>)

3 TERMINOLOGY

3.1 For the purpose of this standard, the definitions given in IS 4167 : 1980 shall apply.

4 ZIRCONIUM SPADNS METHOD

4.1 Principle

Reaction of fluoride with metal ion of metal dye complex like zirconium-SPADNS reagent results in fading in the absorbance of the solution.

4.2 Range and Sensitivity

Zirconium-SPADNS reagent obeys Beer's law over the range from 0.000 μg to 1.40 μg of fluoride per millilitre with a detection limit of the order of 0.02 $\mu\text{g}/\text{ml}$. The method is temperature sensitive and absorbances must be read within $\pm 2^\circ\text{C}$ of the temperature at which the respective calibration curve was established.

4.3 Interferences

Moderate variations in acidity of sample solutions will not interfere. Interferences by aluminium, iron, phosphate and sulphate ion are known — if these are present above the trace level.

4.4 Apparatus

4.4.1 Spectrophotometer

An instrument capable of accepting sample cells of 10 to 25 mm optical path and which is adjustable throughout the visible wavelength region, is required.

4.5 Reagents

4.5.1 Sodium Fluoride Solution

4.5.1.1 Stock solution

Dissolve 2.2105 g of 100 percent sodium fluoride in distilled water and dilute to 1 litre. Store in a polyethylene bottle. 1 ml = 1.0 mg F^- .

4.5.1.2 Working standard solution

Dilute 5.0 ml of the stock solution (4.5.1.1) to 500 ml. Store in a polyethylene bottle. 1 ml = 10 μg F^- .

4.5.2 SPADNS Solution [4, 5 dihydroxy-3-(*p*-sulphophenylazo)-2, 7-naphthalene disulphonic acid trisodium salt]

Dissolve 0.985 g of SPADNS dye in water and dilute to 500 ml.

4.5.3 SPADNS Reference Solution

Add 10 ml of SPADNS solution to 100 ml of water and acidify with a solution prepared by diluting 7 ml of concentrated hydrochloric acid to 10 ml. This solution may be stored and reused repeatedly.

4.5.4 Zirconium Solution

Dissolve 0.265 g of zirconyl chloride octahydrate ($\text{ZrO Cl}_2 \cdot 8\text{H}_2\text{O}$) in 50 ml of water, add 700 ml of concentrated hydrochloric acid and dilute to 1 : 1 with water.

4.5.5 Zirconium — SPADNS Reagent

Mix equal volumes of SPADNS (4.5.2) and zirconium (4.5.4) solutions. Cool to room temperature before use. This reagent may be stored for several months at room temperature in polyethylene container.

4.6 Procedure

4.6.1 Dilute a suitable aliquot of the sample solution to 25 ml and add 5.0 ml of zirconium — SPADNS reagent. Mix and allow to stand for 30 minutes to establish temperature equilibrium before transferring the solution to a spectrophotometer cell. Measure the absorbance value at 570 nm with the spectrophotometer adjusted to read zero absorbance on the SPADNS reference solution.

4.6.2 Calibration and Standards

Prepare a standard series containing from zero to 35 µg of fluoride by pipetting aliquots of the standard fluoride solution into 25 ml volumetric flasks. Add 5 ml of zirconium — SPADNS reagent to each flask, dilute to mark and mix well. Allow the standards to stand for 30 minutes to reach temperature equilibrium at the desired value. Measure absorbances at 570 nm after zeroing the spectrophotometer on the SPADNS reference solution. Prepare a calibration curve relating fluoride concentration, in µg to absorbance values at the selected working temperature.

4.7 Calculation

4.7.1 The concentration of fluoride in air samples are calculated as follows and reported at 25°C and 760 mm Hg pressure:

$$\text{Fluorides, g/m}^3 = \frac{A \times 1\,000 \times V_t}{V \times V_a}$$

where

A = fluoride concentration in the sample from calibration graph, in g;

V = volume of air samples, in litres, at 25°C and 760 mm Hg pressure;

V_t = total volume of absorbing solution, in ml; and

V_a = aliquot taken for analysis, in ml.

NOTE — The HF and F_a concentrations are calculated in ppm at 25°C and 760 mm Hg pressure by following equations:

$$\text{HF, ppm} = \frac{3\,450 \times F \times (273 + t)}{PV}$$

$$F_a, \text{ ppm} = \frac{1\,640 \times F \times (273 + t)}{PV}$$

where

F = fluoride ion in total sample, in mg;

P = sampling pressure, in mm Hg;

V = sample volume; and

t = sampling temperature, in °C.

5 SELECTIVE ION ELECTRODE METHOD

5.1 Principle

Atmospheric samples are taken using midget

impingers containing 0.1 M sodium hydroxide. Samples are diluted to 1:1 with total ionic strength adjustment buffer (TISAB). The diluted samples are analysed using fluoride ion selective electrode.

5.2 Range and Sensitivity

The range and sensitivity have not been established but the recommended range is 0.009 to 95 mg/m³ air.

5.3 Interference

Hydroxide ion is the only significant electrode interference; however, addition of TISAB eliminates this interference. Large amounts of complexing metals such as aluminium may result in low readings even in the presence of TISAB.

5.4 Apparatus

5.4.1 Sampling Equipment

The sampling unit for the impinger collection method consists of the following components:

- a) *Pre-filter Unit* — Consists of the filter media and cassette filter holder,
- b) *Midget Impinger* — Containing the absorbing solution or reagent,
- c) *Pump* — Suitable for delivering desired flow rates. The sampling pump is protected from splash over or water condensation by an absorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.
- d) *Rotameter* — To measure the air flow.
- e) *Fluoride selective ion electrode* — Suitable.
- f) *Reference electrode* — Single function, calomel or silver/silver chloride electrode.
- g) *Millivolt-pH meter* — Expanded scale, capable of measuring to within 0.5 mV.
- h) *Magnetic stirrer*

5.5 Reagents

5.5.1 Acetic Acid — Glacial

5.5.2 Absorbing Solution — 0.1 M sodium hydroxide solution.

5.5.3 Sodium Hydroxide — 5 M solution.

5.5.4 Sodium Chloride

5.5.5 Sodium Citrate

5.5.6 Total Ionic Strength Adjustment Buffer (TISAB)

Take 500 ml of double distilled water in a 1-litre beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride and 0.30 g of sodium citrate. Stir to dissolve. Place the beaker in a water bath (for cooling) and slowly add 5 M sodium hydroxide solution until the pH is between 5.0 and 5.5. Cool to room temperature and pour to a 1 litre volumetric flask and make up to the mark with double distilled water.

5.5.7 Standard Fluoride Solution

Dissolve 4.2 g of sodium fluoride in double distilled water and dilute to 1 litre. This is 10^{-1} M (F) solution [1900 $\mu\text{g F}^-/\text{ml}$]. Store in polyethylene container. Prepare other diluted solutions as follows:

- 10^{-2} M (F) by diluting 10 ml of 10^{-1} M (F) to 100 ml to give 190 $\mu\text{g F}^-/\text{ml}$,
- 10^{-3} M (F) by diluting 10 ml of 10^{-2} M (F) to 100 ml to give 19 $\mu\text{g F}^-/\text{ml}$,
- 10^{-4} M (F) by diluting 10 ml of 10^{-3} M (F) to 100 ml to give 1.9 $\mu\text{g F}^-/\text{ml}$, and
- 10^{-5} M (F) by diluting 10 ml of 10^{-4} M (F) to 100 ml to give 0.19 $\mu\text{g F}^-/\text{ml}$.

5.6 Procedure

5.6.0 All glasswares and plasticwares are cleaned in detergent solution, rinsed with tap water and then rinsed with double distilled water.

5.6.1 Pour 30 ml of absorbing solution into the midjet impinger, using a graduated cylinder to measure the volume. Connect the impinger to vacuum pump and the pre-filter assembly with short flexible tubing. Only minimum length for connecting shall be used. The air being sampled should not be passed through any other tubing or equipment before entering the impinger. Turn on pump to begin sample collection. Care shall be taken to measure flow rate, time and/or volume accurately. The sample shall be taken at a flow rate of 1 to 1.5 litres per minute continuously for 8 hours. After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount of unused absorbing solution and add the washing to impinger. Seal the impinger with a hard, non-reactive stopper. Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship impingers with the stems in, the outlets of the stem should be sealed with parafilm or other non-rubber

covers, and the ground glass joints should be sealed to secure the top tightly.

Care shall be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day. A blank impinger shall be handled as the other samples except that no air is sampled through it. Where a pre-filter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc shall be handled as the other samples except that no air is sampled through and this is labelled as blank.

Transfer the sample from the impinger to a 50 ml polyethylene beaker, add 10 ml of TISAB and dilute to 25 ml with double distilled water. Stir the solution. The fluoride ion electrode and the reference electrode are lowered into the stirred solution and the resulting millivolt (mV) reading recorded after it has stabilized. Prepare a series of fluoride standard solutions by diluting 5 ml of each fluoride standard and 5 ml of TISAB in a clear polyethylene beaker to 25 ml with double distilled water. Insert the fluoride ion electrode into each of the stirred calibration solutions starting with the most dilute solution and record the resulting mV reading to the nearest 0.5 millivolt. Plot the millivolt reading *versus* the fluoride ion concentration of the standard on semi-log graph paper. The fluoride ion concentration in $\mu\text{g/ml}$ is plotted on the long axis. The calibration points should be repeated twice daily.

5.7 Calculation

The concentration of fluoride ($\mu\text{g/ml}$) in the sample solution is obtained from the calibration curve.

5.7.1 Total Fluoride ($\mu\text{g F}^-$) in the Sample

Total fluoride ($\mu\text{g F}^-$) = Concentration of sample ($\mu\text{g/ml}$) \times volume of sample (ml).

5.7.2 The total fluoride $\mu\text{g F}^-$ is divided by the volume in litres of air sampled to obtain concentration in $\text{mg F}^-/\text{m}^3$

$$\text{mg F}^-/\text{m}^3 = \frac{\text{Total } \mu\text{g F}^-}{V_s}$$

or

$$\text{mg F}^-/\text{m}^3 = \mu\text{g F}^-/\text{litre}$$

5.7.2.1 Convert the volume of air sampled to standard condition of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P \text{ bar}}{760} \times \frac{298}{T + 273}$$

where

V_s = volume of air, in litres, at 25°C and 760 mm Hg;

V = volume of air, in litres, as measured;

P bar = barometric pressure, in mm Hg; and

T = temperature of air, in degree centigrade.

5.7.3 The concentration can also be expressed in ppm, defined as μl of component per litre of air

$$\text{ppmF}^- = \mu\text{l F}^- / V_s = \frac{24.45}{MW} \times \mu\text{g F}^- / V_s$$

$$= 1.29 \mu\text{l F}^- / V_s$$

where

24.45 = molar volume at 25°C and 760 mm Hg

MW = 19, weight of fluoride ion, (that is $19 \mu\text{g F}^- = 24.45 \mu\text{l}$ at 25°C, 760 mm Hg).

5.7.3.1 To calculate the concentration of hydrogen fluoride as $\text{mg HF}/\text{m}^3$ or ppm HF , simply multiply the corresponding concentration of F^- by 1.05.

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