

# Australian Standard<sup>®</sup>

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## Methods for sampling and analysis of ambient air

### Method 13.2: Determination of fluorides—Gaseous and acid-soluble particulate fluorides—Manual, double filter paper sampling

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#### PREFACE

This Standard was prepared by the Standards Australia Committee on Methods for Examination of Air to supersede AS 2618.2 — 1984, *Ambient air—Determination of gaseous and particulate fluorides—Selective ion electrode method, Part 2: Gaseous fluorides and acid-soluble particulate fluorides (0.1 µg/m<sup>3</sup> or greater)—Manual, double filter paper sampling*. This Standard is to form part of a series for the determination of fluorides in ambient air and is based on ASTM D3266 — 79, *Methods for automated separation and collection of particulate and acidic gaseous fluoride in the atmosphere (double paper tape sampler method)*. Other methods proposed for the series are for determination of fluorides by automated, double paper tape sampling and sodium acetate coated tube absorption methods.

This edition differs from the 1984 version by the inclusion of additional information on fluoride measurement technique. It has also been reformatted to align with the AS 3580 series of Standards.

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#### FOREWORD

Gaseous and particulate fluorides may be released to the atmosphere from a number of industrial processes. Industries emitting fluorides include aluminium smelters, steel works, power stations and hydrofluoric acid, brick, tile, glass and frit, and superphosphate fertilizer manufacturers. Fluorides are the most phytotoxic of the recognized air pollutants and, at atmospheric concentrations of less than 0.5 µg/m<sup>3</sup>, may cause injury to susceptible plant species.

In view of the relative phytotoxicities of the different forms of fluoride, separate collection and analysis of the particulate and gaseous components is necessary.

In general, the health effects on animals are through ingestion of vegetation contaminated by particulate fluorides whereas the health of vegetation is affected by gaseous fluorides such as hydrogen fluoride, silicon tetrafluoride and fluorosilicic acid.

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#### METHOD

**1 SCOPE** This Standard sets out a method for the collection and separation of acidic gaseous and particulate fluorides from ambient air and their determination using a fluoride ion-selective electrode.

This method is applicable to the measurement of acidic gaseous and acid-soluble particulate fluorides suspended in ambient air at concentrations of 0.1 µg/m<sup>3</sup> and greater.

For a one-day sampling period at a flow rate of 0.83 L/s (approximately 50 L/min), an atmospheric concentration of 0.1  $\mu\text{g}/\text{m}^3$  of hydrogen fluoride in air can be measured with an accuracy of 10%. The detection level can be improved by sampling for longer periods, to a maximum of seven days, but the accumulated particulate matter may interfere with the collection of the gaseous fluorides especially if alumina is present in the particulate matter. The upper limits of determination are 55  $\mu\text{g}/\text{m}^3$  for a one-day sampling period and 7.5  $\mu\text{g}/\text{m}^3$  for a seven-day sampling period (at which point partial neutralization of the alkali-impregnated paper affects the results). The presence of acidic gases other than hydrogen fluoride affects the upper limit of determination.

The resultant determination for a sampling period greater than two days may indicate elevated fluoride particulate levels with depleted fluoride gaseous levels but the total value will be valid (see Clause 6).

NOTES:

- 1 This method is subject to certain interferences. Particulate metallic salts such as those of aluminium, iron, magnesium, calcium and rare-earths collected on the initial filter may retain some or all of the gaseous fluorides. The presence of fluorophosphates or fluoroborates could contribute varying amounts of fluorides as they dissociate unpredictably. Acidic aerosols or gases may neutralize or acidify the alkali-impregnated final filter thus preventing the quantitative collection of acidic gaseous fluorides. Although a citric acid impregnated Whatman No. 52 initial filter paper has been shown to allow passage of gaseous hydrofluoric acid, it may permit passage of fluoride particles smaller than about 1  $\mu\text{m}$ . Hence these may impinge on the alkali impregnated final filter paper. If initial filters of higher retentivity are required for removal of particles of size less than 1  $\mu\text{m}$ , a citric acid impregnated filter of Whatman No. 42 filter paper or equivalent may be used.
- 2 The addition of total ionic strength adjustment buffer (TISAB) eliminates a number of possible interferences. The effects of metallic ions are minimized by complexing agents. Variation in ionic strength is overcome by maintaining a high concentration of sodium chloride in the TISAB solution. The TISAB solution is buffered to pH 5 to 6 to avoid negative interference from the formation of complexes containing fluoride ions and positive interference from hydroxide ions being measured.

**2 REFERENCED DOCUMENTS** The following documents are referred to in this Standard:

AS

- 2162 Code of practice for the use of volumetric glassware  
2164 One-mark volumetric flasks  
2165 Burettes and bulb burettes  
2166 One-mark pipettes  
2922 Ambient air—Guide for the siting of sampling units

**3 PRINCIPLE** Ambient air is drawn through an inlet tube and passed through an acid-impregnated filter (initial filter) to collect particulate fluorides and then through an alkali-impregnated filter (final filter) to collect acidic gaseous fluorides.

The fluorides from the exposed filters are extracted into aqueous solution and determined using a fluoride ion-selective electrode.

**4 REAGENTS**

**4.1 General requirements** Only reagents of recognized analytical reagent grade and only distilled water, or water of equivalent purity, containing less than 0.005  $\mu\text{g}$  of fluoride per millilitre shall be used.

**4.2 Solutions**

**4.2.1 Sodium hydroxide solution (200 g/L)** Dissolve 200 g of sodium hydroxide pellets in water, cool and dilute to 1 L. Store in a plastics container.

**4.2.2 Sodium hydroxide solution (40 g/L)** Transfer 100 mL of sodium hydroxide solution (4.2.1) to a 1 L beaker and dilute to 500 mL. Store in a plastics container.

**4.2.3 Sulfuric acid solution** Cautiously add, with stirring, 28 mL of sulfuric acid ( $\rho_{20}$  1.84 g/mL) to 500 mL of water. Cool and dilute to 1 L.

**4.2.4 Total ionic strength adjustment buffer (TISAB)** Dissolve 57 mL of acetic acid ( $\rho$  201.04 g/mL), 58 g of sodium chloride and 4 g of 1,2-cyclohexylenedinitrilotetra-acetic acid (CDTA) in 500 mL of water. Adjust the pH of the solution to between pH 5 and pH 5.5 by adding sodium hydroxide solution (4.2.1). Cool, dilute to 1 L with water and store in a refrigerator.

**4.2.5 Dilute TISAB solution** Dilute 500 mL of TISAB (4. 2.4) to 1 L with water.

**4.2.6 Alcoholic citric acid solution (21 g/L)** Dissolve 4.2 g of citric acid monohydrate in 200 mL of ethanol (950 mL/L)).

**4.2.7 Alcoholic sodium hydroxide/glycerol solution (20 g/L)** Dissolve 4 g of sodium hydroxide in 200 mL of a solution consisting of 190 mL of ethanol (950 mL/L) and 10 mL of glycerol.

### 4.3 Standard solutions

**4.3.1 Stock fluoride solution** (1 mL  $\equiv$  1 mg HF) Dissolve in 250 mL of water,  $1.050 \pm 0.001$  g of sodium fluoride, previously dried at  $105 \pm 2^\circ\text{C}$  for 1 h. Transfer to a 500 mL volumetric flask and dilute to volume with TISAB (4.2.4). Transfer to a plastics container and store in a refrigerator.

This solution may be usable for up to 12 months if stored in a refrigerator.

**4.3.2 Standard fluoride solution** (1 mL  $\equiv$  20  $\mu\text{g}$  HF) Pipette 10.0 mL of stock fluoride solution (4.3.1) into a 500 mL volumetric flask and dilute to volume with dilute TISAB solution (4.2.5). Prepare freshly before use (see Note 1).

**4.3.3 Dilute working standard fluoride solution** (1 mL  $\equiv$  0.2  $\mu\text{g}$  HF) Pipette 10.0 mL of standard fluoride solution (4.3.2) into a 1 L volumetric flask and dilute to volume with dilute TISAB solution (4.2.5). Prepare freshly before use (see Note 1).

**4.3.4 Working standard fluoride solution** (1 mL  $\equiv$  0.4  $\mu\text{g}$  HF) Pipette 20.0 mL of standard fluoride solution (4.3.2) into a 1 L volumetric flask and dilute to volume with TISAB (4.2.4). Prepare freshly before use (see Note 1).

#### NOTES:

- 1 The standard fluoride solutions may be stored for up to 3 h in a refrigerator provided that they are stored in high-density polycarbonate or polytetrafluoroethylene (PTFE) containers. The standard solutions should be brought to room temperature before use.
- 2 The working standard fluoride solutions are used to spike solutions containing low levels of fluoride so that they can be read from the linear part of the calibration graph. Spiking solutions with fluoride decreases the response time of the fluoride ion-selective electrode.

## 5 APPARATUS

**5.1 Glassware** Grade A volumetric glassware shall be used throughout. Volumetric flasks shall comply with AS 2164, burettes shall comply with AS 2165, and pipettes shall comply with AS 2166. Use of volumetric glassware shall comply with AS 2162.

**5.2 Sampling train (see Figure 1)**—consisting of the components in the following list. The pump and gas meter shall be contained in a ventilated, weatherproof housing.

- (a) *A filter holder (see Figure 2)*—consisting of two blocks of material resistant to fluoride, e.g. nylon, anodized aluminium, stainless steel, PTFE, and containing two stainless steel perforated backing discs, two O-rings and the initial and final filter papers. The blocks shall be bolted together to produce a gas-tight seal.
- (b) *A stand or device*—to support the filter holder with the inlet facing downwards.
- (c) *Durable tubing or hose*—of at least 5 mm internal diameter, sufficient to allow the air flow through the sampling train at the specified rate without collapsing.
- (d) *A diaphragm pump*—capable of maintaining a flow rate of between 0.5 L/s and 1.2 L/s under the conditions of test. It shall be capable of maintaining its performance under continuous use at ambient temperatures up to  $50^\circ\text{C}$ . The exhaust hose connecting the pump to the gas meter should be at least 2 m in length and should be coiled inside the waterproof housing to reduce heat transfer to the pump.
- (e) *A dry gas meter*—of appropriate capacity with a flow rate accuracy of  $\pm 2\%$ .

NOTE: A restrictive orifice of about  $\varnothing 2.5$  mm at the gas meter inlet is useful for reducing pulses in the gas flow.

**5.3 Specific ion meter or expanded scale pH meter**—capable of reading to 0.1 mV.

**5.4 Combination fluoride ion-selective electrode or separate fluoride ion and reference electrodes**

**5.5 Magnetic stirrer and PTFE-coated spin bars**

**5.6 Auto-analyzer** (optional)—fitted with a fluoride ion-selective electrode.

**5.7 Filter papers** A batch of filter papers shall be prepared by dipping them into the appropriate impregnating solution and allowing them to dry in a fluoride-free atmosphere.

CAUTION: PRECAUTIONS ARE NECESSARY TO AVOID FLUORIDE CONTAMINATION OF THE PAPERS FROM THE AIR OR THE HANDS. THE USE OF DISPOSABLE GLOVES AND FORCEPS IS NECESSARY WHEN HANDLING FILTER PAPER AS HUMAN PERSPIRATION CONTAINS FLUORIDES.

The unexposed, final filter papers shall be prepared and treated concurrently with each batch of initial and final filter papers. Prepared filter papers shall be stored in a sealed container to prevent contamination or chemical reaction. The following filter papers are required:

- (a) Initial filter paper, 110 mm diameter medium speed paper which retains crystalline particles or slow speed paper which retains fine crystalline particles, depending on application (see Clause 1 Note 1). The filter shall be impregnated with alcoholic citric acid solution (4.2.6) to collect fluoride particles and to allow the passage of fluoride gases.

NOTE: For the medium speed, crystalline retention filter, Whatman No. 52 filter papers have been found to be suitable. For the slow speed, fine crystalline retention paper, Whatman No. 42 filter papers have been found to be suitable.