

# Australian/New Zealand Standard™

## Methods for sampling and analysis of ambient air

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

#### PREFACE

This Standard was prepared by the joint Standards Australia/Standards New Zealand Committee EV-007, Methods for Examination of Air, to supersede AS 3580.13.2—1991, Method 13.2: *Determination of fluorides—Gaseous and acid-soluble particulate fluorides—Manual, double filter paper sampling*.

This Standard was prepared using ASTM D3266-91, *Standard Test Method for Automated Separation and Collection of Particulate and Acidic Gaseous Fluoride in the Atmosphere (Double Paper Tape Sampler Method)*; ‘Method 207’, *Methods of Air Sampling and Analysis*, Lodge, J.P., 3<sup>rd</sup> edition, 1988; and *Performance of Double Filter Samplers for Ambient Fluoride Monitoring*, Shortland, J.W. et al, Clean Air Society of Australia and New Zealand, 1984.

#### FOREWORD

Gaseous and particulate fluorides may be released to the atmosphere from a number of anthropogenic sources. These include aluminium smelters, steel works, petroleum refineries and power stations, together with manufacturers of hydrofluoric acid, clay products (e.g. bricks and tiles), glass, glass frit and phosphate fertilizer. Fluorides are the most phytotoxic of the recognized air pollutants and, at atmospheric concentrations from as low as 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 phases is necessary.

In general, health effects on animals result from the 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.

## METHOD

### 1 SCOPE

This Standard sets out a method for the collection and separation of gaseous and particulate fluorides from ambient air and their determination using a fluoride ion-selective electrode. Other analytical methods may be used; however, they are outside the scope of this Standard.

This method is applicable to the measurement of gaseous and acid-soluble particulate fluorides suspended in ambient air at concentrations of  $0.020 \mu\text{g}/\text{m}^3$  and greater.

For a 24 h sampling period at a flow rate of  $0.83 \text{ L/s}$  (approximately  $50 \text{ L/min}$ ), an atmospheric concentration of  $0.15 \mu\text{g}/\text{m}^3$  of hydrogen fluoride in air can be measured, with measurement uncertainty of 10%.

The lower limit of detection can be improved by sampling for longer periods, to a maximum of seven days ( $0.020 \mu\text{g}/\text{m}^3$ ); however, the accumulated particulate matter may interfere with the collection of gaseous fluorides, especially if alumina is present in the particulate matter. The upper limits of detection for gaseous fluoride are  $45 \mu\text{g}/\text{m}^3$  for a 24 h sampling period and  $6.5 \mu\text{g}/\text{m}^3$  for a seven day sampling period (at which point partial neutralization of the alkali-impregnated final filter affects the results). The presence of acid gases other than hydrogen fluoride will also reduce the upper limit of detection.

The resultant determination for a sampling period greater than two days may indicate elevated particulate fluoride levels with depleted gaseous fluoride levels but the total value will still be valid (see Clause 7.2).

#### NOTES:

- 1 This method is subject to certain interferences. Particulate metallic salts, such as those of aluminium, iron, magnesium and calcium, or rare-earth elements, collected on the acid-impregnated prefilter 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. If this potential interference is present, the decreased alkalinity of the sample extract may provide relevant information.

Although a citric-acid-impregnated Whatman No. 52 cellulose prefilter (or equivalent) has been shown to allow passage of gaseous hydrofluoric acid, it may permit passage of fluoride particles smaller than approximately  $7 \mu\text{m}$  in equivalent aerodynamic diameter. Hence small particles containing fluoride can impinge on the alkali-impregnated final filter, representing a positive interference on the gaseous fluoride result. A prefilter of higher retentivity is therefore required to remove particles less than  $1 \mu\text{m}$  in equivalent aerodynamic diameter (citric-acid-impregnated Whatman No. 42 cellulose prefilter or equivalent).

- 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 Verification and use of volumetric apparatus
- 2162.1 Part 1: General—Volumetric glassware
- 2164 Laboratory glassware—One-mark volumetric flasks
- 2165 Laboratory glassware—Burettes
- 2166 Laboratory glassware—One-mark pipettes
- 3580 Methods for sampling and analysis of ambient air
- 3580.14 Part 14: Meteorological monitoring for ambient air quality monitoring applications

### AS/NZS

- 3580 Methods for sampling and analysis of ambient air
- 3580.1.1 Part 1.1: Guide to siting air monitoring equipment

### ISO/IEC

- Guide 98-3: Uncertainty of measurement—Part 3: Guide to the expression of uncertainty in measurement (GUM 1995)

### NATA

- Technical Note 8—In-situ calibration of barometers
- Technical Note 19—Liquid-in-glass thermometers—Selection, use and calibration checks

## 3 DEFINITIONS

For the purpose of this Standard, the definitions below apply.

### 3.1 Fluorides

Gaseous, solid or dissolved compounds containing fluorine that result from anthropogenic and natural processes.

### 3.2 Measurement uncertainty

A variable associated with the result of a measurement that characterizes the dispersion of the values that could be reasonably attributed to the measurand.

NOTE: The variable may be, for example, a standard deviation (or given multiple of it), or the half-width of an interval having a stated level of confidence. ISO/IEC Guide 98-3 provides a basis of evaluating uncertainty in the measurement system output.

### 3.3 $U_{95}$

A measurement of uncertainty at a confidence interval of 95% according to ISO/IEC Guide 98-3.

## 4 PRINCIPLE

Ambient air is drawn through an acid-impregnated filter (prefilter) 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. Alternative analytical techniques may be used; however, this should be noted as a nonconformance with this Standard.

## 5 REAGENTS

### 5.1 General requirements

Only reagents of recognized analytical reagent grade, or higher, and distilled water, or water of equivalent purity, containing less than 0.005 µg of fluoride per millilitre, shall be used.

### 5.2 Solutions

#### 5.2.1 Sodium hydroxide solution (200 g/L)

Dissolve 200 g of sodium hydroxide pellets in water, cool and dilute to 1 L with water. Store in a suitable plastic container (see Clause 6.8).

#### 5.2.2 Sodium hydroxide solution (40 g/L)

Transfer 100 mL of sodium hydroxide solution (Clause 5.2.1) to a 1 L beaker and dilute to 500 mL with water. Store in a suitable plastic container (see Clause 6.8).

#### 5.2.3 Sulfuric acid solution

Cautionously add, with stirring, 28 mL of concentrated sulfuric acid (specific gravity 1.84 g/mL) to 500 mL of water. Cool and dilute to 1 L with water.

#### 5.2.4 Total ionic strength adjustment buffer (TISAB)

Dissolve 57 mL of glacial acetic acid (1.049 g/mL), 58 g of sodium chloride and 4.0 g of 1,2-cyclohexylenedinitrilotetraacetic 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 (Clause 5.2.1). Cool, dilute to 1 L with water and store in a refrigerator. Alternatively, commercially available solutions may be purchased.

#### 5.2.5 Dilute TISAB solution

Dilute 500 mL of TISAB (Clause 5.2.4) to 1 L with water.

#### 5.2.6 Alcoholic citric acid solution (21 g/L)

Dissolve 4.2 g of citric acid monohydrate in 200 mL of ethanol (950 mL/L).

#### 5.2.7 Alcoholic sodium hydroxide/glycerol solution (20 g/L)

Dissolve 4.0 g of sodium hydroxide in 20 mL of water and then add 180 mL of a solution consisting of 170 mL of ethanol (minimum 950 mL/L) and 10 mL of glycerol.

### 5.3 Standard solutions

#### 5.3.1 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 (Clause 5.2.4). Transfer to a suitable plastic container (see Clause 6.8) and store in a refrigerator. Alternatively, commercially available solutions may be purchased.

This solution can be retained for up to 12 months if stored in a refrigerator.

#### 5.3.2 Standard fluoride solution (1 mL $\equiv$ 20 µg HF)

Pipette 10.0 mL of stock fluoride solution (Clause 5.3.1) into a 500 mL volumetric flask and dilute to volume with dilute TISAB solution (Clause 5.2.5). Transfer to a high density polyethylene, polypropylene or polytetrafluoroethylene (PTFE) container. The standard fluoride solution should be at room temperature before use.

Prepare fresh daily before use.

### 5.3.3 Dilute working standard fluoride solution ( $1\text{ mL} \equiv 0.2\text{ }\mu\text{g HF}$ )

Pipette 10.0 mL of standard fluoride solution (Clause 5.3.2) into a 1 L volumetric flask and dilute to volume with dilute TISAB solution (Clause 5.2.5). Transfer to a high density polyethylene, polypropylene or polytetrafluoroethylene (PTFE) container. The dilute working standard fluoride solution should be at room temperature before use.

Prepare fresh daily before use.

### 5.3.4 Working standard fluoride solution ( $1\text{ mL} \equiv 0.4\text{ }\mu\text{g HF}$ )

Pipette 20.0 mL of standard fluoride solution (Clause 5.3.2) into a 1 L volumetric flask and dilute to volume with TISAB (Clause 5.2.4). Transfer to a high density polyethylene, polypropylene or polytetrafluoroethylene (PTFE) container. The working standard fluoride solution should be at room temperature before use.

Prepare fresh daily before use.

NOTE: 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.

## 6 APPARATUS

### 6.1 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 2162.1.

### 6.2 Sampling train

The double filter paper sampling train (see Figure 1) consists of the following components, with the pump and gas meter contained in a ventilated, weatherproof housing:

- A filter holder (see Figure 2)—consisting of two blocks of material resistant to fluoride (e.g. nylon, anodized aluminium, stainless steel or PTFE), containing two stainless steel perforated backing discs, two O-rings and the pre and final filters. The blocks shall be screwed together to produce a gas-tight seal.
- A stand or device—to support the filter holder with the inlet facing downwards.
- Durable tubing or hose—of at least 5 mm internal diameter, sufficient to allow air flow through the sampling train at the specified rate without collapsing.
- A pump—capable of maintaining a flow rate of between 30 L/min and 50 L/min under the conditions of test. It shall be capable of maintaining its performance under continuous use at ambient temperatures up to 50°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 dry gas meter.

NOTE: Traditionally diaphragm pumps have been utilized as they have been found reliable and leak free. Piston pumps are generally not suitable due to leakage around piston seals.

- A dry gas meter—of appropriate capacity with a  $U_{95}$  of  $\pm 2\%$  at the sample flow rate.

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

### 6.3 Specific ion meter

Either a specific ion meter or an expanded scale pH meter—capable of reading to 0.1 mV.

### 6.4 Fluoride ion-selective electrode

Either a combination fluoride ion-selective electrode or separate fluoride ion and reference electrodes.

## 6.5 Magnetic stirrer

This shall be equipped with PTFE-coated spin bars.

## 6.6 Auto-analyser (optional)

If used, this shall be equipped with a fluoride ion-selective electrode.

## 6.7 Filter papers

A batch of filters shall be prepared by dipping them into the appropriate impregnating solution and allowing them to dry in a fluoride-free atmosphere (air dried or in a vented drying oven at approximately 50°C).

NOTE: Precautions are necessary to avoid fluoride contamination of the papers from the air or during handling. The use of disposable plastic gloves and stainless steel or PTFE-coated forceps is necessary when handling filters, as human perspiration contains fluorides.

Laboratory and field blank filters shall be prepared and treated concurrently with each batch of pre and final filters. Once dried, each filter shall be examined for pinholes or other defects using a light table. Only filters without defects shall be used for sampling. Filters with defects should be discarded or used for laboratory or field blanks. Inspected filters shall be stored in a sealed container in a fluoride-free environment to prevent contamination or chemical reaction. Treated filters can be stored for a period of up to three months prior to use. The following filters are required:

- (a) Prefilter—110 mm diameter cellulose filter (see Scope, Note 1), impregnated with alcoholic citric acid solution (Clause 5.2.6) to collect particulate fluorides and allow the passage of gaseous fluorides. Whatman No. 42 cellulose filters, or equivalent, shall be used.
- (b) Final filter—110 mm diameter cellulose filter impregnated with alcoholic sodium hydroxide/glycerol solution (Clause 5.2.7) to collect gaseous fluorides. Whatman No. 4 cellulose filters, or equivalent, shall be used.

## 6.8 Plastic beakers and containers

Beakers, solution storage containers and extraction screw-top jars shall be constructed from high density linear polyethylene, polypropylene or PTFE. Petri dishes for storage of sample filters may be constructed from polystyrene.

## 6.9 Flow meter

A traceable reference standard flow measuring device (e.g. calibrated dry or wet gas meter) with a  $U_{95}$  of  $\pm 2\%$  at the operating flow rate.

A traceable transfer standard flow measuring device (e.g. electronic piston meter, dry gas meter or flow meter), with a  $U_{95}$  of  $\pm 2\%$  at the operating flow rate, may be used for field applications. The transfer standard device shall be calibrated against a reference standard device on a two yearly basis.

## 6.10 Light table

A light table to check filters for pinholes or other defects.

## 6.11 Thermometer

A thermometer with a  $U_{95}$  of  $\pm 0.5^\circ\text{C}$ . The thermometer shall be checked against a reference thermometer at  $0^\circ\text{C}$  (ice point), or at one point in the working range, on a six monthly basis (NATA Technical Note 19).

## 6.12 Timing device

A stopwatch or other timing device, capable of measuring elapsed time, with a  $U_{95}$  of  $\pm 1\%$  and a resolution of 1 second. The timing device shall be checked against the recorded time signal, over a minimum period of 1 h, on a six monthly basis.