

# Australian Standard®

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## Methods for sampling and analysis of ambient air

### Method 13.1: Determination of fluorides— Gaseous and acid-soluble particulate fluorides— Automated, double paper tape sampling

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#### PREFACE

This Standard was prepared by the Standards Australia Committee on Methods for Examination of Air to supersede AS 2618.1—1983, *Ambient air—Determination of gaseous and particulate fluorides—Selective ion electrode method, Part 1: Gaseous fluorides and acid-soluble particulate fluorides (1 µg/m<sup>3</sup> or greater)—Automated double paper tape sampling*. This Standard is based on ASTM D 3266 –79, *Methods for automated separation and collection of particulate and acidic gaseous fluoride in the atmosphere (double paper tape sampler method)*.

This Standard is part of a series for the determination of fluorides in ambient air. One other method in the series is published at present and is titled AS 3580.13.2, *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*. Another method proposed for the series is for the determination of gaseous and acid-soluble airborne particulate fluoride by a sodium acetate coated tube absorption method.

This Standard differs from the 1983 edition by the inclusion of additional information on fluoride measurement technique and information on the precision of measurement. 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 fluoride 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 produced 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.

## METHOD

**1 SCOPE** This Standard sets out a method for the collection and separation of acidic gaseous and acid-soluble 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  $1 \mu\text{g}/\text{m}^3$  and greater.

### 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 tape 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 tape thus preventing the quantitative collection of acidic gaseous fluorides. Although a citric acid impregnated Whatman No. 52 initial filter tape 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 tape. If initial tapes of higher retentivity are required for removal of particles of size less than  $1 \mu\text{m}$ , citric acid impregnated tapes 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 paper tape (initial filter tape) to collect particulate fluorides and then through an alkali-impregnated paper tape (final filter tape) to collect acidic gaseous fluorides. The sampler is programmed to collect and store samples over selected time periods of up to 3 h.

The fluorides from the exposed filter tapes 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 plastic 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 plastic 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 ( $\rho_{20}$  1.04 g/mL), 58 g of sodium chloride and 4 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 (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°C for 1 h. Transfer to a 500 mL volumetric flask and dilute to volume with TISAB (4.2.4). Transfer to a plastic 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  $\mu$ 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  $\mu$ 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  $\mu$ 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 polyethylene, 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 Sampler** (Figure 1)—consisting of a vacuum pump which draws air in series through two adjacent filter tapes separated by a polytetrafluoroethylene gasket (see Figure 2) in a sampling block. Provision shall be made for advancing the filter tapes automatically after a preselected period. The sampler shall have two supply reels and two take-up reels with appropriate capstans to guide the tapes through the sampling block.