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., 3rd 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^3, 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 µg/m^3 and greater.

For a 24 h sampling period at a flow rate of 0.83 L/s (approximately 50 L/min), an atmospheric concentration of 0.15 µg/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 µg/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 µg/m^3 for a 24 h sampling period and 6.5 µg/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 µm 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 µm 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.