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**Workplace atmospheres — Determination of inorganic acids by ion chromatography —**

Part 3: **Hydrofluoric acid and particulate fluorides**

*Air des lieux de travail — Détermination des acides inorganiques par chromatographie ionique —*

*Partie 3: Acide fluorhydrique et fluorures particulaires*

CD

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](https://www.iso.org/directives-and-policies.html)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](https://www.iso.org/iso-standards-and-patents.html)).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see [www.iso.org/iso/foreword.html](https://www.iso.org/foreword-supplementary-information.html).

This document was prepared by Technical Committee ISO/TC 146, Air quality, Subcommittee SC 2, Workplace atmospheres.

This second edition cancels and replaces the first edition (ISO 21438-3:2010), which has been technically revised.

The main changes are as follows:

— in total, new format by using the actual template;

— in total, deleted subclauses and write it as paragraphs where possible;

— clause 2, updated;

— clause 3, reduced to necessary by mention ISO 18158;

— clause 6, removed the reagents for electronically suppressed ion chromatography;

— clause 8, reduced by mention relevant standards;

— clause 9, new Figure 1;

— clause 10, deleted subclause “Setting up the instrument”.

A list of all parts in the ISO 21438 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](https://www.iso.org/members.html).

Introduction

The health of workers in many industries is at risk through exposure by inhalation of hydrofluoric acid and particulate fluorides. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure, and this is generally achieved by making workplace air measurements. This document has been published in order to make available a method for making valid exposure measurements for hydrofluoric acid and particulate fluorides in use in industry. It is intended for agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users of hydrofluoric acid and particulate fluorides, and their workers.

The execution of the provisions and the interpretation of the results obtained with the use of this document are entrusted to appropriately qualified and experienced people.

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**Workplace atmospheres — Determination of inorganic acids by ion chromatography —**Part 3: **Hydrofluoric acid and particulate fluorides**

# Scope

This document specifies a method for the determination of the time-weighted average mass concentration of soluble particulate fluorides and hydrofluoric acid (HF) in workplace air by collection of the particulate fluorides on a pre-filter and HF on an alkali-impregnated filter and analysis by ion chromatography.

This method is only applicable to determination of particulate fluorides that are soluble using the sample preparation procedure specified.

For aerosol sampling, this method is applicable to the personal sampling of the inhalable fraction of airborne particles, as defined in ISO 7708, and to static (area) sampling.

The method is applicable to the determination of masses of 0,005 mg to at least 1,25 mg of particulate fluorides per sample and 0,012 5 mg to at least 1,2 mg of HF per sample.

The concentration range of particulate fluorides and HF in air for which the measuring procedure is applicable is determined by the sampling method selected by the user. For a 120 l air sample, the working range is approximately 0,04 mg/m³ to at least 10 mg/m³ for particulate fluorides and approximately 0,13 mg/m³ to at least 10 mg/m³ for HF.

HF can react with co-sampled particulate matter on the pre-filter, causing an interference on the measured concentration.

# Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696*, Water for analytical laboratory use; Specification and test methods*

ISO 7708, *Air quality — Particle size fraction definitions for health-related sampling*

ISO 8655‑1, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO 8655‑2, *Piston-operated volumetric apparatus — Part 2: Piston pipettes*

ISO 8655‑6, *Piston-operated volumetric apparatus — Part 6: Gravimetric methods for the determination of measurement error*

ISO 18158, *Workplace air – Terminology*

ISO 20581, *Workplace atmospheres — General requirements for the performance of procedures for the measurement of chemical agents*

ISO 21832:2018, *Workplace air — Metals and metalloids in airborne particles – Requirements for evaluation of measuring procedures*

# Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

* ISO Online browsing platform: available at <https://www.iso.org/obp>
* IEC Electropedia: available at <https://www.electropedia.org/>

3.1

blank solution

solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample dissolution

3.2

calibration blank solution

calibration solution prepared without the addition of any working standard solution

NOTE The concentration of fluoride in the calibration blank solution is taken to be zero.

3.3

calibration solution

solution prepared by dilution of the working standard solution, containing an analyte at concentrations that are suitable for use of the analytical instrument calibration blank

3.4

extraction solution

solvent or solution used to solubilise the analyte(s) of interest

3.5

sample dissolution

process of obtaining a solution containing fluoride from a sample, which might or might not involve complete dissolution of the sample

3.6

sample solution

solution prepared from a sample by the process of sample dissolution

NOTE A sample solution can require further operations, for example dilution, in order to produce a test solution that is ready for analysis.

3.7

stock standard solution

process of obtaining a solution containing fluoride from a sample, which might or might not involve complete dissolution of the sample

3.8

test solution

blank solution or sample solution that has been subjected to all operations required to bring it into a state in which it is ready for analysis

NOTE The blank test solution is the blank solution and the sample test solution is the sample solution if these solutions are not subjected to any further operations before analysis

3.9

### working standard solution

solution, prepared by dilution of the stock standard solution, that contains fluoride at a concentration that is better suited for preparation of calibration solutions than the concentration of fluoride in the stock standard solution

# Principle

A known volume of air is drawn through a pre‑filter and an alkali-impregnated filter mounted in an inhalable sampler (7.1.1) to collect particulate fluorides and HF. Particulate fluorides are collected on the pre‑filter and HF is collected on the alkali-impregnated filter.

The pre‑filter and alkali-impregnated filter are extracted separately with water or eluent (see 10.1.1), without heating, to solubilize the fluorides.

Aliquots of the sample solution are subjected to ion chromatography in order to separate the extracted fluoride from other anions. Following this separation, fluoride is measured using a conductivity detector.

Analytical results are obtained by plotting the measured conductivity as a function of concentration. They can be used for assessment of occupational exposure to fluorides and HF in air.

# Requirements

The measuring procedure shall comply with the performance requirements of ISO 20581 and/or any relevant International, European or National Standard that specifies performance requirements of procedures for measuring chemical agents in workplace air.

# Reagents

## General

Use only reagents of recognized analytical grade and only water as specified in 6.1. It is advisable to check the blank values of all chemicals before use.

NOTE The presence of acetate or formate in reagents can cause a significant interference on fluoride detection. It is therefore advisable to check that all reagents to be used have a negligible acetate and formate content.

## Water, from a purification system that delivers ultrapure water of grade 1 in accordance with the requirements of ISO 3696

NOTE: State of art water purification systems deliver water of grade 1 with higher quality than specified in ISO 3696 (e.g. resistivity greater than 18 MΩ•cm).

## Sodium carbonate (Na2CO3), anhydrous, greater than 99,9 % mass fraction.

### Sodium carbonate impregnation solution.

|  |  |  |  |
| --- | --- | --- | --- |
| Diameter Filter | Concentration | Impregnation Volume | Reference |
| 37 mm | 0,75 mol/l | 240 µL | [17] |
| 37 mm | 50 g/l | 500 µL | [18] |

Note: It could be necessary to adjust the concentration and volume of impregnation by using another sampler with different size of filter. However, the amount of sodium carbonate have to be the same.

## Fluoride standard solutions.

### Fluoride stock standard solution.

Use a commercial standard solution with a certificate of its concentration, for example 1 000 mg/l, traceable to national standards. Observe the manufacturer's expiry date or recommended shelf-life. If necessary, dilute the standard solution (e.g., from 1 000 mg/l to 100 mg/l) to prepare the stock solution.

### Fluoride calibration solutions

Pipette appropriate volumes of the stock solution to create the calibration. The calibration range shall be in accordance with the calculated working range described in ISO 21832:2018, 5.2.1, and the limit of quantification described in ISO 21832:2018, 8.1.2. A multi-point (the number of points to be consistent with the quality system of the laboratory) calibration shall be constructed within the linear range of the analytical method.

### Fluoride check-standard

Use a Certified Reference Material (CRM) as described in 10.4.3 with a certificate of its concentration, for example 100 mg/l for fluoride, traceable to national standards. Observe the manufacturer's expiry date or recommended shelf-life.

### Fluoride check-standard working solution

The check-standard working solution should be in the middle of the calibration range. Pipette a proper volume of 6.3.3 to create a check-standard with the water (6.1). Prepare this solution fresh for every calibration. If necessary, create a check-standard working solution for fluoride separately.

# Apparatus

## Sampling equipment

### Samplers, designed to collect the inhalable fraction of airborne particles, suitable for mounting a pre-filter and an alkali-impregnated filter separated by a spacer, manufactured from a material that does not react with HF.

Note 1 If samplers have an internal filter cassette, this shall also be manufactured from a material that does not react with HF.

NOTE 2 Materials which do not react with acids, from which samplers and internal filter cassettes can be manufactured, include polytetrafluoroethylene (PTFE) and other fluorinated polymers, polyvinyl chloride (PVC), polyethylene, polypropylene and polycarbonate.

NOTE 3 Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge that can be removed from the sampler to enable this material to be easily recovered.)

### Filters, of a diameter suitable for use with the samplers (7.1.1).

#### Pre-filters, for sampling particulate fluorides, with a collection efficiency ≥ 99 % for particles with a 0,3 µm diffusion diameter, manufactured from a material that does not react with HF.

Refer to B.1 for guidance on suitable materials from which pre‑filters can be manufactured.

#### Sampling-filters, for sampling HF, impregnated with sodium carbonate, for example 37 mm diameter cellulose nitrate filters impregnated with 240 µl of 0,75 mol/l sodium carbonate solution (6.3.1) (see Reference [17]), dried in a dessicator for a minimum of 8 h; or 37 mm diameter binder-free quartz fibre filters impregnated with 500 µl of 50 g/l sodium carbonate solution (6.3.1) (see Reference [18]).

Refer to B.2 for guidance on materials from which HF sampling filters can be manufactured.

### Spacers, of a diameter suitable for use with the samplers (7.1.1) for separating the pre‑filters (7.1.2.1) and HF sampling filters (7.1.2.2), manufactured from an inert material that does not react with the acids and on which the acids are not adsorbed, for example polypropylene sleeves, PTFE-coated screens or polystyrene rings.

### Sampling pumps, in accordance with ISO 13137[11]should be used

If the sampling pump is used outside the range of conditions specified in ISO 13137[11] appropriate action should be taken to ensure that the performance requirements are met. For instance, at sub-zero temperatures it might be necessary to keep the pump warm.

### Flowmeter, portable, with an accuracy that is sufficient to enable the volumetric flow rate to be measured to within ±5 %.

The calibration of the flowmeter shall be checked against a primary standard, i.e. a flowmeter whose accuracy is traceable to national standards. If appropriate (see 9.1.3), record the atmospheric temperature and pressure at which the calibration of the flowmeter was checked.

It is advisable that the flowmeter used be capable of measuring the volumetric flow rate to within ±2 % or better.

### Ancillary equipment

* Flexible tubing, for example silicone of an outer diameter of 10 mm and an inner diameter of 6 mm for making a leakproof connection from the samplers to the sampling pumps without compressing as a result of the pressure difference between ambient atmosphere and the in-line vacuum at the used flow rate of 1 l min−1.
* Belts or harnesses, which the sampling pump can conveniently fix for personal sampling.
* Tweezers, manufactured from or tipped with PTFE, for handling filters.
* Filter transport cassettes, or similar, if required (see 9.5), in which to transport samples to the laboratory.
* Thermometer, of range 0 °C to 50 °C, graduated in divisions of at least 1 °C or less, for measurement of atmospheric temperature. For applications at temperatures below freezing, the range of the thermometer shall extend to the appropriate desired range.
* Barometer, suitable for measurement of atmospheric pressure, if required.

## Laboratory apparatus

CAUTION**— Fluorides are found ubiquitously in the environment. This can lead to elevated blanks so it is especially important to take great care that all disposable plastic labware is checked for fluoride contamination and that all reusable laboratory apparatus is thoroughly clean before use.**

### Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

### Plastic labware.

* One-mark volumetric flasks**,** for example polymethylpentene (PMP)
* Screw-cap polyethylene vessels**,** proper for the extraction of collected sample filters.
* Beakers, of appropriate capacity.
* Disposable membrane filters, of PTFE, of pore size 0.45 µm, for use in ion chromatography.
* Disposable syringes, of appropriate capacity, appropriate needles.
* Autosampler vials, of appropriate capacity.

### Piston-operated volumetric instruments, of capacities of 50 µl to 10 ml, complying with the requirements of ISO 8655-1, and tested in accordance with ISO 8655-6; pipettors, complying with the requirements of ISO 8655-2, as an alternative to one-mark pipettes for the preparation of standard solutions, calibration solutions and dilution of samples.

### Ultrasonic bath, preferably with a timer, suitable for use in the ultrasonic extraction method for soluble particulate fluorides and hydrofluoric acid.

### Ion chromatograph, having the following listed components inclusive. Components and tubing that come into contact with the sample solution or eluent shall, as far as possible, be comprised of inert materials, for example polyetheretherketone (PEEK).

* Pump, capable of delivering a constant flow within the range 0.1 mL/min to 5 mL at a pressure of 15 MPa to 150 MPa.
* Eluent generation system, for producing an eluent suitable for use with the selected separator column, as an alternative to use of a manually prepared eluent (e.g. see Reference [19]).
* Sample injection system, comprising a low dead-volume, non-metallic valve fitted with a sample loop, for injecting the sample solution into the eluent stream.
* Guard and separator column**,** packed with high capacity pellicular anion exchange resin, suitable for resolving sulfates and phosphates from other inorganic anions.
* Suppressor module (chemically suppressed or electronically suppressed) for ion chromatography,suitable for use with the separator column.
1. **Conductivity detector**, flow through, low volume, with a non-metallic flow path.

# Occupational exposure assessment

Refer to relevant international, European or national standards (e.g. ISO 20581, EN 689[10], ASTM E1370[7]) for guidance on how to develop an appropriate assessment strategy and for general guidance on measurement strategy.

# Sampling

## Preliminary considerations

### Selection and use of samplers

Select samplers (7.1.1) according to the requirements of the applicable limit value. Size selective samplers shall collect the appropriate fraction of airborne particles as defined in ISO 7708 and confirmed by testing (e.g. using EN 13205[26]). If possible, the samplers selected should be manufactured from conducting material, since samplers manufactured from non-conducting material have electrostatic properties that can influence representative sampling.

Use the samplers at their design flow rate and in accordance with the instructions provided by the manufacturer. See CEN/TR 15230[9] for further guidance.

### Sampling period

Select a sampling period that is appropriate for the measurement task (see Clause 8) but ensure that it is long enough to enable particulate fluorides and HF to be determined with acceptable uncertainty at levels of industrial hygiene significance. When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the filter with particulate matter. For example, estimate the minimum sampling time, *t*min, in minutes, required to ensure that the amount collected is above the lower limit of the working range of the analytical method when particulate fluorides or HF are present in the test atmosphere at the appropriate multiple of its limit value (i.e. 0,1 times for an 8 h time-weighted average limit value or 0,5 times for a short-term limit value), using Formula (1):

 (1)

where

*t*min is the minimum sampling time, in minutes;

*m*LOQ is the limit of quantification, given as mass of the analyte on the sampling substrate, in micrograms;

*q*V is design flow rate, in litres per minute, of the sampler;

*k* is the appropriate multiple of the limit value (0,1 times for an 8 h time-weighted average limit value or 0,5 times for a short-term limit value);

*ρ*LV is the limit value, in milligrams per cubic metre.

If the minimum sampling time is not short enough for the method to be useful for the intended measurement task, consider the possibility of using a sampler designed to be used at a higher flow rate.

When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the pre-filter with particulate matter.

When a high concentration of HF is anticipated, select a sampling period that is not so long as to risk exceeding the maximum sampling capacity of the HF sampling filter. See Reference [17] and [18].

### Effect of temperature and pressure on flow rate measurements

Refer to the manufacturer’s instructions to determine whether the indicated volumetric flow rate of the flowmeter (7.1.5) is dependent upon temperature and pressure. Consider whether the difference between the atmospheric temperature and pressure at the time of calibration of the flowmeter and during sampling is likely to be great enough to justify making a correction to take this into account, for example if the error could be greater than ±5 %. If a correction is necessary, measure and record the atmospheric temperature and pressure at which the calibration of the flowmeter was checked, and measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 9.4).

NOTE 1 An example of temperature and pressure correction for the indicated volumetric flow rate is given in Clause A.1 for a constant pressure drop, variable area flowmeter.

Consider whether it is necessary to recalculate the concentration of particulate fluorides and (HF) in air to reference conditions (see ISO 8756[2]). If so, measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 9.4) and use the formula given in A.2to apply the necessary correction.

NOTE 2 The concentration of HF in air is generally stated for actual environmental conditions (temperature, pressure) at the workplace. If the concentration is to be compared with occupational exposure limit values that are referenced at normal temperature and pressure, then the concentration should be stated at normal temperature and pressure.

### Sample handling

To minimize the risk of damage or contamination, only handle the pre‑filters, HF sampling filters, and spacers in a clean area where the concentration of HF and particulate fluorides in air is as low as possible and only handle filters using tweezers.

## Preparation for sampling

### Cleaning of samplers

Clean the samplers (7.1.1) before use,. Dismantle the samplers, soak in detergent solution, rinse thoroughly with water (6.1), wipe with absorbent tissue and allow to dry before reassembling. Alternatively, use a laboratory washing machine.

Note: Some samplers are single use and disposable and may not require cleaning before use.

### Loading the samplers with filters

Load each clean sampler first with an impregnated sampling filter (7.1.2.2), then with a pre‑filter (7.1.2.1), separated with a spacer (7.1.3). A spacer may also be placed behind the HF sampling filter to support it. Ensure that the configuration in which the filters are loaded leads to the sampled air passing first through the pre-filter and then through the impregnated filter (see Figure 1). Label each sampler so that it can be uniquely identified and seal with its protective cover or plug to prevent contamination.



**Key**

1 pre-filter

2 spacer (required)

3 impregnated sampling filter

4 spacer (optional)

5 direction of air flow through the sampler

Figure 1 — Filter loading configuration

### Setting the volumetric flow rate

Perform the following in a clean area, where the concentrations of particulate fluorides and HF are minimal.

Connect each loaded sampler to a sampling pump (7.1.4) using flexible tubing (7.1.6), ensuring that no leaks can occur. Remove the protective cover or plug from each sampler, switch on the sampling pump, attach the flowmeter (7.1.5) to the sampler so that it measures the flow through the sampler inlet orifice(s) and set the required volumetric flow rate. Switch off the sampling pump and seal the sampler with its protective cover or plug to prevent contamination during transport to the sampling position.

If necessary, allow the sampling pump operating conditions to stabilize before setting the volumetric flow rate.

### Field blanks

Retain as blanks one unused loaded sampler from each batch of 10 prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position but draw no air through the filters.

## Sampling position

### Personal sampling

Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, for example fastened to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, for example to a belt around the waist, or place it in a convenient pocket.

Give consideration to whether the nature of the process is likely to result in a significant difference between the actual exposure of the worker and the concentration of particulate fluorides and HF measured by a sampler mounted on the lapel. If this is the case, make special arrangements to mount the sampler as close as possible to the worker's nose and mouth.

### Static sampling

If static sampling is carried out to assess the exposure of a worker in a situation where personal sampling is not possible, position the sampler in the immediate vicinity of the worker and at breathing height. If in doubt, take the sampling position to be the point where the risk of exposure is considered to be greatest.

If static sampling is carried out to characterize the background level of particulate fluorides and HF in the workplace, select a sampling position that is sufficiently remote from the work processes, such that results are not directly affected by particulate fluorides and HF from emission sources.

## Collection of samples

When ready to begin sampling, remove the protective cover or plug from the sampler and switch on the sampling pump. Record the time and volumetric flow rate at the start of the sampling period. If the sampling pump is fitted with an integral timer, check that this is reset to zero. Measure the atmospheric temperature and pressure at the start of the sampling period using the thermometerand barometer (7.1.6) and record the measured values.

NOTE If the temperature or pressure at the sampling position is different from that where the volumetric flow rate was set (see 9.2.3), the volumetric flow rate could change and can require re-adjustment before sampling.

At the end of the sampling period (see 9.1.2), record the time and calculate the duration of the sampling period. Check the malfunction indicator or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout thesampling period. Measure the volumetric flow rate at the end of the sampling period using the flowmeter and record the measured value. Measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer and barometer and record the measured values.

Carefully record the sample identity and all relevant sampling data (see 13). Calculate the mean volumetric flow rate by averaging the volumetric flow rates at the start and at the end of the sampling period and, if appropriate (see 9.1.3), calculate the mean atmospheric temperature and pressure. Calculate the volume of air sampled, in litres, at atmospheric temperature and pressure, by multiplying the mean flow rate, in litres per minute, by the duration, in minutes, of the sampling period.

If the post-sampling verification of flow rate is within ±5 % of the measured value prior to sampling, then it is possible to use the pre-sampling volumetric flow rate or to calculate the mean volumetric flow rate by averaging the volumetric flow rates at the start and at the end of the sampling period

If the post-sampling flow rate differs by more than 5 % from the pre-sampling flow rate, the sample should either be considered invalid, or flagged with calculation of concentrations using both flow rate values and consideration of both values. However, samplers of selective size fractions are required to operate within a ±5 % range of a nominal flow rate so the sample shall be considered invalid since a pre- to post-sampling deviation of greater than ±5 % will be outside of the allowed range.

## Transportation

### Samplers that collect airborne particles and/or gases on the filter

For samplers that collect airborne particles and/or gases on the filter (see NOTE 4 to 7.1.1), remove the filter from each sampler, place in a labelled filter transport cassette (7.1.6) and close with a lid. Alternatively, transport samples to the laboratory in the samplers in which they were collected. Take particular care to prevent the collected sample from coming into contact with the walls of the transport container.

### Sampler with an internal filter cassette

For samplers with an internal filter cassette (see NOTE 4 to 7.1.1), remove the filter cassette from each sampler and fasten with its lid or transport clip.

### Samplers of the disposable cassette type

For samplers of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

### Transport of samples to the laboratory

Transport the samples to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to ensure proper handling.

Ensure that the documentation which accompanies the samples is suitable for a “chain of custody” to be established (e.g. see ASTM D4840[8]).

# Analysis

## General

**CAUTION**— Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) while carrying out the analysis.

## Preparation of test and calibration solutions

### Selection of sample preparation method

Decide whether to use water (6.1) or eluent (depending on the analytical technique and separator column used) to prepare test solutions for determination of particulate fluorides and HF.

### Preparation of test solutions

Open each filter cassette or sampler (see 9.5) and transfer both filters into individual, labelled screw-cap vessels or beakers using clean tweezers (7.2.2), ensuring that the side of the pre‑filter on which the particulate fluoride sample was collected is facing upwards. Follow the same procedure for the blank filters (see 9.2.4).

Pipette 5,0 ml of water (6.1) or eluent (10.1.1) into each screw-cap vessel or beaker.

Swirl gently to mix the contents, ensuring that the filter remains completely immersed. Sonicate for 15 min in an ultrasonic bath and then allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally.

Filter each sample solution through a PTFE filter, for example by using a disposable syringe, dispensing each filtrate into an individual, labelled, autosampler vial (see 7.2.2).

### Preparation of calibration solutions

Prepare a minimum of five calibration solutions to cover a concentration range, for example from 0,8 mg/l to 8 mg/l of fluoride. Accurately pipette appropriate volumes of fluoride stock solution (6.3.1) into individual, labelled plastic one-mark volumetric flasks (7.2.2), dilute to the mark, close and mix thoroughly. Prepare these calibration solutions fresh daily.

## Instrument analysis

### Analysis

Inject the calibration solutions (10.1.3) into the ion chromatography system in order of increasing concentration and measure fluoride peaks for each calibration solution, in peak area mode.

Use the instrument's computer to generate a calibration function using a linear regression. Repeat the calibration if the coefficient of determination, r2, is not greater than 0,999.

NOTE 1 If r2 <0,999, it can be possible to remove an erroneous calibration point and reprocess the data to obtain an acceptable calibration.

Inject the blank and sample test solutions (10.1.2) into the ion chromatography system and make measurements for each solution. Use the stored calibration function to determine the fluoride concentrations in milligrams per litre.

Analyse the calibration blank and a mid-range calibration solution after the initial calibration and then after every 10 test solutions. If the measured concentration of fluoride in the continuing calibration blank (CCB) is above the method limit of detection (LOD), as determined in 10.3.2, or if the measured concentration of fluoride in the continuing calibration verification (CCV) has changed by more than ±5 %, take one of the following corrective measures. Either use the instrument software to correct for the sensitivity change (reslope facility) or suspend analysis and recalibrate the instrument. In either case, reanalyse the test solutions that were analysed during the period in which the sensitivity change occurred or, if this is not possible, reprocess the data to take account of the sensitivity change.

Analyse reagent blank solutions and laboratory blank solutions as specified in 10.4.1, and quality control solutions as specified in 10.4.2. Use the results to monitor the performance of the method as specified in 10.4.2.

If concentrations of fluoride are found to be above the upper limit of the linear calibration range, dilute the test solutions in order to bring them within the linear range and repeat the analysis. Add an appropriate volume of extraction solution when making dilutions so that the diluted test solutions and the calibration solutions are matrix matched, and record the dilution factor, fdilution.

NOTE 2 For samples expected to have very high concentrations of fluoride, it can requiredilution of the test solutions before they are first analysed.

## Estimation of detection and limits of quantification (LOQs)

### Estimation of the instrumental limit of detection

Estimate the instrumental LOD under the working analytical conditions following the procedure described and repeat this exercise whenever the experimental conditions are changed significantly.

NOTE The instrumental LOD is of use in identifying changes in instrument performance, but it is not a method LOD (see Reference [20]). The instrumental LOD is likely to be lower than the method LOD, because it only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample.

Prepare a test solution with fluoride concentrations near the anticipated instrumental LODs by diluting the working standard solution (6.3.1) by an appropriate factor. Make at least 10 ion chromatographic measurements on the test solution and calculate the instrumental LOD as three times the sample standard deviation of the mean concentration value.

### Estimation of the method limits of detection and limits of quantification

Estimate the method LODs and LOQs under the working analytical conditions following procedure (which is based upon the approach described in Reference [21]) and repeat this exercise whenever the experimental conditions are changed significantly.

Fortify at least 10 pre‑filters (7.1.2.1) and at least 10 HF sampling filters (7.1.2.2) with fluoride near the anticipated LODs, for example 1 µg of fluoride, by spiking each filter with 0,01 ml of a solution prepared by diluting the stock standard solution or check-standard (6.3) by an appropriate factor. Prepare test solutions following the sample dissolution procedure used to prepare the sample test solutions (see 10.1.2).

Make ion chromatographic measurements on the test solutions derived from each spiked filter and calculate the method LOD and the LOQ as 3 times and 10 times the sample standard deviation of the mean concentration value, respectively, for each filter type. The results for the pre‑filter give the method LOD and the LOQ for the determination of particulate fluoride and the results for the HF sampling filter give the method LOD and the LOQ for the determination of HF.

NOTE An alternative procedure for estimating the method LOD involves the analysis of filter samples fortified with the analyte of interest at values spanning the predicted LOD (see Reference [20]).

## Quality control

### Reagent blanks and laboratory blanks

Carry reagent blanks and laboratory blanks through the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Prepare reagent blank solutions and laboratory blank solutions at a frequency of at least one per 20 samples or a minimum of one per batch.

If results for reagent blanks and/or laboratory blanks are significantly higher than expected, based on previous experience, investigate whether contamination is occurring from laboratory activities and/or the batch of filters used for sampling and take appropriate corrective action to ensure that this does not re-occur.

### Quality control solutions

Carry spiked samples and spiked duplicate samples throughout the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percentage recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of filters to which known amounts of fluoride have been added. (This can be accomplished by spiking with known volumes of fluoride working standard solution at amounts within the linear dynamic range of the instrument. The working fluoride standard solution used shall be prepared from a stock standard fluoride solution from a different source than that used for preparing the calibration solutions.) Process these quality control samples according to a frequency of at least 1 in 20 samples or a minimum of one per batch.

Monitor the performance of the method by plotting control charts of the relative percentage recoveries and of the relative percentage differences between the spiked samples and the spiked duplicate samples. If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action, and reanalyse the samples if necessary. See ASTM E882[6] for general guidance on the use of quality control charts.

### Certified reference materials

## Suitable certified reference materials (CRMs) for fluoride shall be analysed prior to routine use of the method to establish that the percentage recovery relative to the certified value is satisfactory.Measurement uncertainty

It is recommended that laboratories estimate and report the uncertainty of their measurements in accordance with ISO/IEC Guide 98-3:2008[4]. The first step is to construct a cause and effect diagram[3]to identify the individual sources of random and systematic error in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of two is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 References [23]and [24] describe the application of cause and effect analysis to analytical methods.

NOTE 2 Terms that contribute to the random variability of the method are generally accounted for in the measurement precision, which can be determined from quality control data. Error associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the drift permitted before the instrument is recalibrated (10.2) by √3.

NOTE 3 Systematic errors include those associated with method recovery, sample recovery, preparation of working standard solutions, dilution of test solutions, etc.

# Expression of results

Calculate the mass concentration of HF and particulate fluorides in the air samples at ambient conditions, using Equations (2) and (3):

 (2)

 (3)

where

*ρ*HF is the mass concentration, in milligrams per cubic metre, of HF, as fluoride, in the air sample;

*ρ*F is the mass concentration, in milligrams per cubic metre, of particulate fluorides, as fluoride, in the air sample;

*ρ*F,0 is the mean concentration, in milligrams per litre, of fluoride in the blank test solutions;

*ρ*F,1 is the concentration of fluoride, in milligrams per litre, in the sample test solution;

*V* is the volume, in litres, of the air sample;

*V*0 is the volume, in millilitres, of the blank test solution;

*V*1 is the volume, in millilitres, of the sample test solution;

*f*dilution is the dilution factor (*f*dilution = 1 in the absence of dilution);

*f*conversion is the factor to convert from anion to acid concentration (1,053).

# Method performance (Reference [17])

## Sampling efficiency and sample storage

### HF

Laboratory testing with test atmospheres of HF has determined the sampling efficiency to be >95 % for HF in the range of 0,3 mg/m3 to 5 mg/m3 at humidities of up to 60 %.

Results lower 0,3 mg/m³ determined a recovery of 87 %.

At a humidity of 80 %, the sampling efficiency decreases to 60 %, see 12.1.3.

Recovery of HF was >95 % after two weeks sample storage.

### Particulate fluorides

Laboratory testing with filters spiked with fluoride yielded a recovery of >95 % after four weeks sample storage.

### Humidity

The humidity is tested according to ISO 22065 (8.3.3.3) [27]for particulate fluorides and HF.

For particulate fluoride no influence was determined.

For HF an influence was determined at humidities of more than 60 %. At a humidity of 80 % a recovery of 60 % was determined. In the range of 60 % - 80 % humidity the recovery decreases. By plotting the recovery against the relative humidity in a linear regression the result can corrected with a recovery depending on the humidity by the following formula.

 (4)

Where

*H*rel.relative humidity at the measurement

Fhumidity result recovery depending on the humidity

## Limit of quantification

The target values for LOQs depend on the applicable local limit value. In accordance with ISO 20581, it is preferred that limits of quantification are at least one-tenth or lower than the mass collected at the limit value concentration in a sample volume associated with the applicable averaging time of the limit value and the maximum flow rate of the method.

The LOQ of the method has been determined (see Reference [17]) to be 3,0 mg/l for HF and 1,0 mg/l for particulate fluorides. For a sample solution volume of 5 ml and an air sample volume of 120 l, this is approximately equivalent to 0,13 mg/m3 for HF and 0,04 mg/m3 for particulate fluorides.

## Upper limits of the working range

The upper limit of the working range of the method for HF is governed by the maximum permissible loading of the HF sampling filters. It has been demonstrated that no breakthrough occurs at sample loadings of up to 1,2 mg (equivalent to 4 h sampling at an HF concentration of 5 mg/m3 for a sample volume of 240 l).

## Bias and precision

### Analytical bias

Laboratory experiments have shown that the analytical method does not exhibit significant bias. The mean analytical recovery, determined from the analysis of spiked filters, has been found (see Reference [17]) to be in the range (100 ± 2) % for HF and particulate fluorides.

### Analytical precision

The component of the coefficient of variation of the method that arises from analytical variability, *CV* (analysis), determined from the analysis of test gas samples for HF and from spiked samples for particulate fluorides, has been found (see Reference [17]) to be in the range 1,1 % to 3,1 % for HF and 0,3 % to 3,8 % for particulate fluorides.

## Uncertainty of sampling and analysis method

The expanded uncertainty of the method, using a coverage factor of 2, has been estimated (see Reference [17]) to be <20 % for HF and <22 % for particulate fluorides.

## Interferences

Formate and acetate cause a significant interference on fluoride detection. Therefore, substances in the sampled air that could lead to the presence of formate or acetate in the sample solutions cause a positive interference. In such circumstances, analysis using a fluoride ion selective electrode is a suitable alternative.

# Test report

The test report shall contain all information required by the end user, regulatory authorities and accreditation organizations, including at least the following:

1. a statement to indicate the confidentiality of the information supplied, if appropriate;
2. a complete identification of the air sample, including the date of sampling, the place of sampling, the type of sample (personal or static), either the identity of the individual whose breathing zone was sampled (or other personal identifier) or the location at which the general occupational environment was sampled (for a static sample), a very brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;
3. a reference to this document, i.e. ISO 21438-3;
4. the make, type, and diameter of filters used;
5. the make and type of sampler used;
6. the make and type of sampling pump used, and its identification;
7. the make and type of flowmeter used, the primary standard against which the calibration of the flowmeter was checked, the range of flow rates over which the calibration of the flowmeter was checked, and the atmospheric temperature and pressure at which the calibration of the flowmeter was checked, if appropriate (see 9.1.3);
8. the times, in minutes, of the start and the end of the sampling period, and the duration of the sampling period;
9. the mean flow rate, in litres per minute, during the sampling period;
10. the mean atmospheric temperature and pressure during the sampling period, if appropriate (see 9.1.3);
11. the volume, in litres, of air sampled at ambient conditions;
12. the name of the person who collected the sample;
13. the time-weighted average mass concentration, in milligrams per cubic metre, as fluoride, of HF or particulate fluorides found in the air sample at ambient temperature and pressure, or, if appropriate, adjusted to reference conditions;
14. the analytical variables used to calculate the result, including the concentrations of fluoride in the sample and blank solutions, the volumes of the sample and blank solutions, and the dilution factor, if applicable;

NOTE If necessary data (e.g. the volume of air sampled) are not available to the laboratory for the above calculations to be carried out, the laboratory report can contain the analytical result in micrograms of HF or micrograms of particulate fluorides per filter sample.

1. the type(s) of instrument(s) used for sample preparation and analysis, and unique identifier(s);
2. the estimated instrumental LODs, method LODs and LOQs under the working analytical conditions, the measurement uncertainty determined in accordance with ISO/IEC Guide 98‑3[4]; and, if requested by the customer, quality control data;
3. any operation not specified in this document, or regarded as optional;
4. the name of the analyst(s) [or other unique identifier(s)];
5. the date of the analysis;
6. any inadvertent deviations, unusual occurrences, or other notable observations.
7. (informative)

Temperature and pressure correction
	1. Temperature and pressure correction for the indicated volumetric flow rate

Bubble flowmeters and frictionless piston flowmeters are preferred for measuring the volumetric flow rate because the readings they give are independent of temperature and pressure. For other flowmeters including orifice and thermal mass flowmeters, it may be necessary to apply a correction to the indicated volumetric flow rate, if the temperature and pressure at the time of measurement is different to when the calibration of the flowmeter was checked.

A typical example of the need for a temperature and pressure correction is when a constant-pressure drop, variable-area, flowmeter is used to measure the volumetric flow rate. In this instance, use Equation (A.1) to calculate a corrected air sample volume, *V*corr, in litres:

 (A.1)

where

*q*V is the mean flow rate, in litres per minute;

*t* is the sampling time, in minutes;

*p*1 is the atmospheric pressure, in kilopascals, during calibration of the sampling pump flowmeter;

*p*2 is the mean atmospheric pressure, in kilopascals, during the sampling period;

*T*1 is the temperature, in kelvin, during calibration of the sampling pump flowmeter;

*T*2 is the mean temperature, in kelvin, during the sampling period.

A theoretical calculation shows that a 5 % deviation in the air sample volume at the reference atmospheric pressure of 101,3 kPa occurs at 91,9 kPa and 112,2 kPa. Both these values are outside the normal weather conditions at sea level, but this pressure difference corresponds to an altitude change of about 800 m (−0,1 kPa ≈ 8 m increased altitude) at normal atmospheric pressure at sea level. Similarly, a 5 % deviation in the air sample volume at the reference temperature of 293 K occurs at 264 K and 323 K.

Any other flowmeter can also require a correction for variation in pressure and temperature. Follow the manufacturer's instructions for such corrections.

* 1. Recalculation of HF in air concentrations to reference conditions

If necessary (see 9.1.3), recalculate the mass concentrations, in milligrams per cubic metre, as fluoride, corrected to reference conditions (e.g. 293 K and 101,3 kPa) in the air sample of HF, *ρ*HF,corr, and particulate fluorides, *ρ*F,corr, using Equations (A.2) and (A.3):

 (A.2)

 (A.3)

where

*ρ*HF *is the concentration, in milligrams per cubic metre, of HF as fluoride in the air sample, at ambient conditions;*

*ρ*F *is the concentration, in milligrams per cubic metre, of particulate fluorides as fluoride in the air sample, at ambient conditions;*

*T*2 *is the mean temperature, in kelvin, during the sampling period;*

*p*2 *is the mean atmospheric pressure, in kilopascals, during the sampling period;*

*293 is the reference temperature (20 °C), expressed in kelvin;*

*101,3 is the reference atmospheric pressure, in kilopascals.*

1. (informative)

Filter materials
	1. Pre-filters

The purpose of the pre‑filters is to collect particulate fluorides and separate them from HF. In some workplaces, HF can be present partially as a mist, i.e. in the form of an aerosol. In such circumstances, mist droplets are first trapped on the pre-filters and then, during the course of sampling, HF vaporizes and is subsequently collected on the alkali-impregnated cellulose nitrate filters.

HF is a powerful acid that reacts with many filter materials, notably silica-based materials such as glass fibre and quartz fibre. Therefore correct selection of the pre‑filter used for collection of particulate fluorides is of paramount importance. In particular, the pre-filter shall be manufactured from a material that does not react with HF. Also, the filters used shall not be manufactured from a material that can release acetate or formate (e.g. cellulose acetate), since this can interfere with the chromatographic analysis (see 12.6).

Membrane filters manufactured from PTFE and other fluorinated polymers, PVC, mixed cellulose esteror cellulose nitrate, with a pore size of 5 µm or less, are generally suitable for use as pre‑filters. Quartz fibre and glass fibre filters are unsuitable as they react with HF. However, the level and variability of blanks can vary significantly depending on the filter supplier and the individual filter batch. It is therefore advisable to verify that each batch of filters is fit for use by determining the LOQ following the procedure prescribed in 10.3.2.

* 1. HF sampling filters

Filters made from many polymeric materials cannot be used to prepare HF sampling filters because they have hydrophobic properties that make them unsuitable for impregnation with sodium carbonate solution. Also, the filters used shall not be manufactured from a material that can release acetate or formate (e.g. cellulose acetate), since this can interfere with the chromatographic analysis (see 12.6). The use of cellulose nitrate filters, mixed cellulose ester filter or quartz fibre filters is recommended. However, for cellulose nitrate filters and mixed cellulose ester filter, the level and variability of blanks can vary significantly depending on the supplier and the individual filter batch.

It is advisable to check that the level and variability of fluoride on cellulose nitrate filters and mixed cellulose ester filter are low before impregnation with sodium carbonate solution and to verify that each batch of HF sampling filters prepared is fit for use by determining the LOQ following the procedure prescribed in 10.3.2.

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