INTERNATIONAL STANDARD

**ISO 21438-3**

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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*



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# Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 21438-3 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

ISO 21438 consists of the following parts, under the general title *Workplace atmospheres — Determination of inorganic acids by ion chromatography*:

— *Part 1: Non volatile acids (sulfuric acid and phosphoric acid)*

— *Part 2: Volatile acids, except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid)*

— *Part 3: Hydrofluoric acid and particulate fluorides*

## 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 part of ISO 21438 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. It has been assumed in the drafting of ISO 21438 (all parts) that the execution of its provisions and the interpretation of the results obtained are entrusted to appropriately qualified and experienced people.

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

## Part 3: Hydrofluoric acid and particulate fluorides



## 1 Scope

This part of ISO 21438 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.

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

For aerosol sampling, the 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 $m^{-3}$ to at least 10 mg $m^{-3}$ for particulate fluorides and approximately 0,13 mg $m^{-3}$ to at least 10 mg $m^{-3}$ for HF.

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

## 2 Normative references

The following referenced documents are indispensable for the application 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 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3585, *Borosilicate glass 3.3 — Properties*

ISO 7708:1995, *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*

EN 13205, *Workplace atmospheres — Assessment of performance of instruments for measurement of airborne particles*

# 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

## 3.1 General definitions

**3.1.1**
**breathing zone**
〈general definition〉 space around the worker's face from where he or she takes his or her breath

NOTE Adapted from EN 1540:—[13], 2.4.5.

**3.1.2**
**breathing zone**
〈technical definition〉 hemisphere (generally accepted to be 0,3 m in radius) extending in front of the human face, centred on the midpoint of a line joining the ears; the base of the hemisphere is a plane through this line, the top of the head and the larynx

NOTE 1 The definition is not applicable when respiratory protective equipment is used.

NOTE 2 Adapted from EN 1540:—[13], 2.4.5.

**3.1.3**
**chemical agent**
any chemical element or compound, on its own or admixed as it occurs in the natural state or as produced, used or released including release as waste, by any work activity, whether or not produced intentionally and whether or not placed on the market

[Council Directive 98/24/EC[17] Art. 2(a)]

**3.1.4**
**exposure by inhalation**
situation in which a chemical agent is present in the air that is inhaled by a person

NOTE Adapted from EN 1540:—[13], 2.4.1.

**3.1.5**
**occupational exposure limit value**
limit of the time-weighted average of the concentration of a chemical agent in the air within the breathing zone of a worker in relation to a specified reference period

[Council Directive 98/24/EC[17], Art. 2(d)]

EXAMPLES Threshold Limit Values® (TLVs) established by the ACGIH (Reference [18]) and indicative occupational exposure limit values (IOELVs) promulgated by the European Commission (Council Directive 2006/15/EC[19]).

**3.1.6**
**measurement procedure for the sampling and analysis of chemical agents in air**
**measuring procedure for the sampling and analysis of chemical agents in air**
set of operations, described specifically, used for the sampling and analysis of chemical agents in air

NOTE A measuring procedure for the sampling and analysis of chemical agents in air usually includes the following steps: preparation for sampling, sampling, transportation and storage, preparation of samples for analysis and analysis.

**3.1.7**
**operating time**
period during which a sampling pump can be operated at specified flow rate and back pressure without recharging or replacing the battery

NOTE Adapted from EN 1232:1997[12], 3.5.

**3.1.8**
**reference period**
specified period of time for which the limit value of a chemical agent applies

NOTE 1 The reference period is usually 8 h for long-term measurements and 15 min for short-term measurements.

NOTE 2 Adapted from EN 1540:—[13], 2.4.7.

**3.1.9**
**workplace**
defined area or areas in which the work activities are carried out

[EN 1540:—[13], 2.5.2]

## 3.2 Particle size fraction definitions

**3.2.1**
**inhalable convention**
target specification for sampling instruments when the inhalable fraction is the fraction of interest

[ISO 7708:1995, 2.4]

**3.2.2**
**inhalable fraction**
mass fraction of total airborne particles which is inhaled through the nose and mouth

NOTE The inhalable fraction depends on the speed and direction of air movement, on breathing rate and other factors.

[ISO 7708:1995, 2.3]

**3.2.3**
**respirable convention**
target specification for sampling instruments when the respirable fraction is of interest

[ISO 7708:1995, 2.12]

**3.2.4**
**respirable fraction**
mass fraction of inhaled particles which penetrate to the unciliated airways

[ISO 7708:1995, 2.11]

**3.2.5**
**total airborne particles**
all particles surrounded by air in a given volume of air

NOTE Because all measuring instruments are size-selective to some extent, it is often impossible to measure the total airborne particle concentration.

[ISO 7708:1995, 2.13]

## 3.3 Sampling definitions

**3.3.1**
**air sampler**
device for separating chemical agents from the surrounding air

NOTE 1 Air samplers are generally designed for a particular purpose, e.g. for sampling gases and vapours or for sampling airborne particles.

NOTE 2 Adapted from EN 1540:—[13], 3.2.1.

**3.3.2**
**personal sampler**
sampler, attached to a person, that collects gases, vapours or airborne particles in the breathing zone to determine exposure to chemical agents

[EN 1540:—[13], 3.2.2]

**3.3.3**
**personal sampling**
process of sampling carried out using a personal sampler

[EN 1540:—[13], 3.3.3]

**3.3.4**
**static sampler**
**area sampler**
sampler, not attached to a person, that collects gases, vapours or airborne particles at a particular location

[EN 1540:—[13], 3.2.3]

**3.3.5**
**static sampling**
**area sampling**
process of air sampling carried out in a particular location

[EN 1540:—[13], 3.3.4]

## 3.4 Analytical definitions

**3.4.1**
**analysis**
all operations carried out after sample preparation to determine the amount or concentration of the analyte(s) of interest present in the sample

NOTE Adapted from EN 14902:2005[16], 3.1.1.

**3.4.2**
**blank solution**
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample dissolution

**3.4.3**
**calibration blank solution**
calibration solution prepared without the addition of any working standard solution

NOTE 1 The concentration of fluoride in the calibration blank solution is taken to be zero.

NOTE 2 Adapted from EN 14902:2005[16], 3.1.3.

**3.4.4**
**calibration solution**
solution prepared by dilution of the working standard solution, containing an analyte at concentrations that are suitable for use in calibration of the analytical instrument

NOTE 1 Adapted from EN 14902:2005[16], 3.1.4.

NOTE 2 For the purposes of this part of ISO 21438, the analyte is fluoride.

**3.4.5**
**field blank**
filter that is taken through the same handling procedure as a sample, except that it is not used for sampling, i.e. it is loaded into a sampler, transported to the sampling site and then returned to the laboratory for analysis

**3.4.6**
**laboratory blank**
unused filter, taken from the same batch used for sampling, that does not leave the laboratory

**3.4.7**
**linear dynamic range**
range of concentrations over which the calibration curve for fluoride is linear

NOTE The linear dynamic range extends from the detection limit to the onset of calibration curvature.

**3.4.8**
**reagent blank**
all reagents used in sample dissolution, in the same quantities used for preparation of laboratory blank, field blank and sample solutions

**3.4.9**
**sample dissolution**
process of obtaining a solution containing fluoride from a sample, which might or might not involve complete dissolution of the sample

NOTE Adapted from EN 14902:2005[16], 3.1.25.

**3.4.10**
**sample preparation**
all operations carried out on a sample, after transportation and storage, to prepare it for analysis, including transformation of the sample into a measurable state, where necessary

NOTE Adapted from EN 14902:2005[16], 3.1.24.

**3.4.11**
**sample solution**
solution prepared from a sample by the process of sample dissolution

NOTE 1 A sample solution might need to be subjected to further operations, e.g. dilution, in order to produce a test solution that is ready for analysis.

NOTE 2 Adapted from EN 14902:2005[16], 3.1.22.

**3.4.12**
**stock standard solution**
solution, used for preparation of the calibration solutions, containing fluoride at a certified concentration that is traceable to national standards

NOTE Adapted from EN 14902:2005[16], 3.1.26.

**3.4.13**
**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 1 “Ready for analysis” includes any required dilution. If a blank solution or sample solution is not subject to any further operations before analysis, it is a test solution.

NOTE 2 Adapted from EN 14902:2005[16], 3.1.30.

**3.4.14**
**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

NOTE Adapted from EN 14902:2005[16], 3.1.32.

## 3.5 Statistical terms

**3.5.1**
**analytical recovery**
ratio of the mass of analyte measured in a sample to the known mass of analyte in that sample

NOTE The analytical recovery is usually expressed as a percentage.

[EN 1540:—[13], 5.1.1]

**3.5.2**
**bias**
difference between the expectation of a test result or measurement result and a true value

NOTE 1 Bias is the total systematic error as contrasted to random error. There can be one or more systematic error components contributing to the bias. A larger systematic difference from the true value is reflected by a larger bias value.

NOTE 2 The bias of a measuring instrument is normally estimated by averaging the error of indication over an appropriate number of repeated measurements. The error of indication is the "indication of a measuring instrument minus a true value of the corresponding input quantity".

NOTE 3 In practice, the accepted reference value is substituted for the true value.

[ISO 3534-2:2006[1], 3.3.2]

NOTE 4 In the case of measurement procedures for the sampling and analysis of chemical agents in air, the accepted reference value can be, for example, the certified value of a reference material, the concentration of a standard test atmosphere or the target value of an interlaboratory comparison.

**3.5.3**
**coverage factor**
$k$
numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

NOTE A coverage factor, $k$, is typically in the range from 2 to 3.

[ISO/IEC Guide 98-3:2008[4], 2.3.6]

**3.5.4**
**combined standard uncertainty**
$u_c$
standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[ISO/IEC Guide 98-3:2008[4], 2.3.4]

**3.5.5**
**expanded uncertainty**
quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

[ISO/IEC Guide 98-3:2008[4], 2.3.5]

**3.5.6**
**precision**
closeness of agreement between independent test/measurement results obtained under stipulated conditions

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

NOTE 3 Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[ISO 3534-2:2006[1], 3.3.4]

**3.5.7**
**true value**
value which characterizes a quantity or quantitative characteristic perfectly defined in the conditions which exist when that quantity or quantitative characteristic is considered

NOTE The true value of a quantity or quantitative characteristic is a theoretical concept and, in general, cannot be known exactly.

[ISO 3534-2:2006[1], 3.2.5]

**3.5.8**
**uncertainty (of measurement)**
parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 The parameter may be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of a series of measurements, and can be characterized by standard deviations. The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information. ISO/IEC Guide 98-3:2008[4] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

## 4 Principle

**4.1** 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.

**4.2** The pre-filter is extracted with water or eluent (see 10.1.1), without heating, to solubilize the particulate fluorides.

**4.3** The alkali-impregnated filter is extracted with water or eluent (see 10.1.1), without heating, to solubilize HF.

**4.4** 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.

**4.5** 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.

## 5 Requirement

The measuring procedure shall comply with any relevant International, European or National Standard that specifies performance requirements of procedures for measuring chemical agents in workplace air (e.g. EN 482[10]).

## 6 Reagents

During the analysis, use only reagents of recognized analytical grade and only water as specified in 6.1.

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.

**6.1 Water**, from a purification system that delivers ultrapure water having a resistivity greater than 0,18 MΩ·m (usually expressed by manufacturers of water purification systems as 18 MΩ cm).

**6.2 Sodium carbonate** ($Na_2CO_3$), anhydrous, >99,9 % mass fraction.

**6.2.1 Sodium carbonate impregnation solution**.

**6.2.1.1 Sodium carbonate solution**, 2,0 mol $l^{-1}$, for impregnation of 25 mm diameter cellulose nitrate filters.

Dissolve 21,2 g $Na_2CO_3$ in water. Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (7.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

**6.2.1.2 Sodium carbonate solution**, 0,75 mol $l^{-1}$, for impregnation of 37 mm diameter cellulose nitrate filters.

Dissolve 7,95 g $Na_2CO_3$ in water. Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (7.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

**6.2.1.3 Sodium carbonate solution**, 50 g $l^{-1}$, for impregnation of 37 mm diameter quartz fibre filters.

Dissolve 5,0 g $Na_2CO_3$ in water. Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (7.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

**6.2.2 Sodium carbonate solution**, for dilution of standards.

Introduce 2,7 ml of sodium carbonate impregnation solution (6.2.1) into a 500 ml one-mark volumetric flask (7.2.2.2) and make up to the mark with water.

**6.3 Cartridge for generation of eluent for chemically suppressed ion chromatography**.

Cartridge, suitable for use with the eluent generation system (7.2.6.2).

**6.4 Reagents for electronically suppressed ion chromatography**.

NOTE The phthalic acid and borate/D-gluconate solutions prescribed below are two examples of eluents used in analysis of fluoride using electronically suppressed ion chromatography. The column manufacturer's literature gives information on the composition of the eluent to be used with a specific column type.

**6.4.1 Phthalic acid** ($C_8H_6O_4$), >99,5 % mass fraction.

**6.4.2 Acetonitrile** ($C_2H_3N$), HPLC grade.

**6.4.3 Methanol** ($CH_3OH$), HPLC grade.

**6.4.4 Lithium hydroxide monohydrate** ($LiOH \cdot H_2O$), >99,5 % mass fraction.

**6.4.5 Boric acid** ($H_3BO_4$), >99,8 % mass fraction.

**6.4.6 D-Gluconic acid solution**, approximately 50 % mass fraction of D-gluconic acid ($C_6H_{12}O_7$) in water.

**6.4.7 Glycerol** ($C_3H_8O_3$), >99 % mass fraction.

**6.4.8 Phthalic acid eluent stock solution**, 0,1 mol $l^{-1}$ phthalic acid in a 9 + 1 volume ratio mixture of acetonitrile and methanol.

Dissolve 16,6 g of phthalic acid (6.4.1) in 900 ml of acetonitrile (6.4.2) and 100 ml of methanol (6.4.3), in a suitable 1 l vessel and mix thoroughly.

**6.4.9 Lithium hydroxide solution**, 1 mol $l^{-1}$.

Dissolve 4,2 g of lithium hydroxide monohydrate (6.4.4) in water (6.1). Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (7.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

**6.4.10 Phthalic acid eluent solution**, e.g. 0,005 mol $l^{-1}$ phthalic acid, pH 4,9.

Transfer an appropriate volume, e.g. 50 ml, of phthalic acid solution (6.4.8) to a 1 l beaker (7.2.2.1), add approximately 800 ml of water (6.1), swirl to mix and adjust to pH 4,9 with lithium hydroxide solution (6.4.9). Quantitatively transfer the solution into a 1 l one-mark volumetric flask (7.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

The instructions for preparation of the extraction and eluent stock solution given in 6.4.8 are only an example. If the manufacturer of the separator column recommends the use of a different eluent, it is necessary to prepare a stock solution with a correspondingly different composition. In this case, follow the manufacturer's instructions for eluent preparation.

**6.4.11 Borate and D-gluconate eluent stock solution**.

Dissolve 17 g of boric acid (6.4.5), 4,8 g of lithium hydroxide monohydrate (6.4.4), 8,8 ml of D-gluconic acid (6.4.6) and 62,5 ml of glycerol (6.4.7) in water (6.1). Quantitatively transfer the solution into a 500 ml one-mark volumetric flask (7.2.2.2), dilute to the mark with water, stopper and mix thoroughly.

**6.4.12 Borate and D-gluconate eluent solution**.

Transfer 15 ml of borate and D-gluconate stock solution (6.4.11) and 120 ml of acetonitrile (6.4.2) to a 1 l one-mark volumetric flask (7.2.2.2), dilute to the mark with water (6.1), stopper and mix thoroughly.

The instructions for preparation of the extraction and eluent stock solution given in 6.4.11 are only given as an example. If the manufacturer of the separator column recommends the use of a different eluent, it is necessary to prepare a stock solution with a correspondingly different composition. In this case, follow the manufacturer's instructions for eluent preparation.

**6.5 Fluoride standard solutions**.

**6.5.1 Fluoride stock standard solution**.

Use a commercial standard solution with a certified fluoride concentration, e.g. 1 000 mg $l^{-1}$ of fluoride, traceable to national standards. Observe the manufacturer's expiration date or recommended shelf-life.

**6.5.2 Fluoride working standard solution**, 100 mg $l^{-1}$ of fluoride.

Accurately pipette appropriate volumes, e.g. 2 ml, of the fluoride stock standard solution (6.5.1) into a 20 ml plastic one-mark volumetric flask (7.2.3.1), dilute to the mark with water (6.1), stopper and mix thoroughly. Prepare this solution fresh monthly.

# 7 Apparatus

## 7.1 Sampling equipment

**7.1.1 Samplers**, designed to collect the inhalable fraction of airborne particles, complying with EN 13205, suitable for mounting a pre-filter (7.1.2.1) and an alkali-impregnated filter (7.1.2.2) separated by a spacer (7.1.3), manufactured from a material that does not react with HF.

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

NOTE 1 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 2 CEN/TR 15230:2005[9] gives examples of inhalable samplers with the potential to meet the requirements of EN 13205 that were or had been available on the market up to 2004, including published reports on their performance.

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

**7.1.2.1 Filters**, pre-filters for sampling particulate fluorides, with a collection efficiency of not less than 99,5 % mass fraction for particles with a 0,3 µm diffusion diameter (see ISO 7708:1995, 2.2), 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.

**7.1.2.2 Filters**, for sampling HF, impregnated with sodium carbonate, e.g. 25 mm diameter cellulose nitrate filters impregnated with 100 µl of 2,0 mol $l^{-1}$ sodium carbonate solution (6.2.1.1) or 37 mm diameter cellulose nitrate filters impregnated with 250 µl of 0,75 mol $l^{-1}$ sodium carbonate solution (6.2.1.2) (see Reference [20]), dried in a dessicator for a minimum of 8 h, or 37 mm diameter quartz fibre filters impregnated with 500 µl of 50 g $l^{-1}$ sodium carbonate solution (6.2.1.3) (see Reference [21]).

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

**7.1.3 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, e.g. polypropylene sleeves or PTFE-coated screens.

**7.1.4 Sampling pumps**, with an adjustable flow rate, capable of maintaining the selected flow rate (see 9.1.1.2) to within ±5 % of the nominal value throughout the sampling period (see 9.1.2).

For personal sampling the pumps shall be capable of being worn by the worker without impeding normal work activity.

The pump should have, as a minimum, the following features:

— an automatic control that keeps the volumetric flow rate constant in the case of a changing back pressure;

— either a malfunction indicator which, following completion of sampling, indicates that the air flow has been reduced or interrupted during sampling or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted;

— a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (e.g. screwdriver) or requires special knowledge for operation (e.g. via software), so as to preclude inadvertent readjustment of the flow rate during use.

An integral timer is a highly desirable additional feature.

A flow-stabilized pump may be required to maintain the flow rate within the specified limits.

EN 1232[12] and EN 12919[14] require that the performance of the pumps be such that:

— the pulsation of the flow rate does not exceed 10 %;

— a flow rate set within the nominal range does not deviate by more than ±5 % from the initial value under increasing back pressure;

— within the range of ambient temperatures from 5 °C to 40 °C, the flow rate measured under operating conditions does not deviate by more than ±5 % from the flow rate at 20 °C;

— the operating time is at least 2 h, and preferably 8 h;

— the flow rate does not deviate by more than ±5 % from the initial value during the operating time.

If the sampling pump is used outside the range of conditions specified in EN 1232[12] or EN 12919[14], 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.

**7.1.5 Flowmeter**, portable, with an accuracy that is sufficient to enable the volumetric flow rate (see 9.1.1.2) 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.

**7.1.6 Ancillary equipment**.

**7.1.6.1 Flexible tubing**, of a diameter suitable for making a leakproof connection from the samplers (7.1.1) to the sampling pumps (7.1.4).

**7.1.6.2 Belts** or **harnesses**, to which the sampling pump can conveniently be fixed for personal sampling (except where the sampling pumps are small enough to fit in workers' pockets).

**7.1.6.3 Tweezers**, manufactured from or tipped with PTFE, for loading and unloading filters into samplers (see 9.2.2 and 10.1.2.1).

**7.1.6.4 Thermometer**, range 0 °C to 50 °C, graduated in divisions of at least 1 °C, for measurement of atmospheric temperature, if required (see 9.1.3). For applications at temperatures below freezing, the range of the thermometer shall extend to the appropriate desired range.

**7.1.6.5 Barometer**, suitable for measurement of atmospheric pressure, if required (see 9.1.3).

## 7.2 Laboratory apparatus

Ordinary laboratory apparatus and in particular the following.

**7.2.1 Disposable gloves**, impermeable, to protect the hands from contact with toxic and corrosive substances. PVC gloves are suitable.

**7.2.2 Glassware**.

**7.2.2.1 Beakers**, of suitable capacities between 100 ml and 1 l, made of borosilicate glass 3.3 complying with the requirements of ISO 3585, cleaned before use with water (6.1).

**7.2.2.2 One-mark volumetric flasks**, of suitable capacities between 100 ml and 1 l, complying with the requirements of ISO 1042 class A, made of borosilicate glass 3.3 complying with the requirements of ISO 3585, cleaned before use with water (6.1).

Alternatively, the flasks may be cleaned with a suitable laboratory detergent using a laboratory washing machine and rinsed thoroughly with water.

**7.2.3 Plastic labware**.

**7.2.3.1 One-mark volumetric flasks**, of suitable capacities between 10 ml and 1 l.

**7.2.3.2 Screw-cap polyethylene vessels**, disposable, of a suitable capacity, e.g. 10 ml.

**7.2.3.3 Beakers**, of a suitable capacity, e.g. 50 ml.

**7.2.3.4 Graduated centrifuge tubes**, with caps, of a suitable capacity, e.g. 15 ml.

**7.2.3.5 Filter funnels**, of a size suitable for transferring washings from the internal surfaces of the sampler (7.1.1) into a tube.

**7.2.3.6 Disposable filters**, PTFE, pore size 0,45 µm, for use in ion chromatography.

**7.2.3.7 Disposable syringes**, of a suitable capacity, e.g. 2 ml or 5 ml, with luer lock connector, for use with disposable filters (7.2.3.6).

**7.2.3.8 Autosampler vials**, of a suitable capacity, e.g. 1,5 ml to 2 ml.

**7.2.4 Piston-operated volumetric instruments**, complying with the requirements of ISO 8655-1 and tested in accordance with ISO 8655-6: including pipettors, with capacities of 10 µl to 5 ml, complying with the requirements of ISO 8655-2, for the preparation of standard solutions, calibration solutions and dilution of samples.

**7.2.5 Ultrasonic bath**, preferably with a timer, suitable for use in the extraction of particulate fluorides and HF.

**7.2.6 Ion chromatograph**, having the components listed in 7.2.6.1 to 7.2.6.10. Components and tubing that come into contact with the sample solution or eluent shall, as far as possible, be composed of inert materials, e.g. polyether ether ketone (PEEK).

**7.2.6.1 Pump**, capable of delivering a constant flow within the range 0,1 ml $min^{-1}$ to 5 ml $min^{-1}$ at a pressure of 15 MPa to 150 MPa.

**7.2.6.2 Eluent generation system**, for producing an eluent suitable for use with the selected separator column (7.2.6.5) (see for example Reference [22]).

**7.2.6.3 Sample injection system**, consisting of a low dead-volume, electronically metallic valve fitted with a sample loop having a volume of up to 500 µl, for injecting the sample solution into the eluent stream.

**7.2.6.4 Guard column**, placed before the separator column (7.2.6.5) to protect it from fouling by particles or strongly adsorbed organic constituents of the sample solution.

**7.2.6.5 Separator column**.

**7.2.6.5.1 Separator column for chemically suppressed ion chromatography**, packed with high-capacity pellicular anion exchange resin, suitable for resolving fluorides from other inorganic anions.

**7.2.6.5.2 Separator column for electronically suppressed ion chromatography**, packed with silica or organic polymers, suitable for resolving fluorides from other inorganic anions.

**7.2.6.6** **Suppressor module for chemically suppressed ion chromatography**, suitable for use with the separator column (7.2.6.5.1).

**7.2.6.7** **Conductivity detector**, flow-through, low volume, with an electronically metallic flow path.

NOTE A conductivity detector can be used with both chemically suppressed and electronically suppressed ion chromatography.

**7.2.6.8** **UV-vis detector**, flow-through, low volume.

NOTE A UV-vis detector can be used with electronically suppressed ion chromatography for inverse UV detection.

**7.2.6.9** **Recorder**, **integrator** or **computer**, compatible with detector output, capable of recording detector response as a function of time, for the purpose of measuring peak height or area. The use of an automated system is recommended.

**7.2.6.10** **Container**, suitable for use as a reservoir for storing eluent or water used for eluent generation (7.2.6.2).

**7.2.7** **pH-meter**.

# 8 Occupational exposure assessment

## 8.1 General

This part of ISO 21438 pertains to the taking of personal and static samples. Refer to relevant International, European or National Standards (e.g. EN 482[10], EN 689[11], and ASTM E1370[7]) for guidance on how to develop an appropriate assessment strategy and for general guidance on measurement strategy.

## 8.2 Personal sampling

Exposure of workers to HF and particulate fluorides shall normally be determined by personal sampling, since the concentration of HF and particulate fluorides in the breathing zone can be different from the background level in the workplace.

## 8.3 Static sampling

Static sampling may be carried out, if appropriate, to assess the exposure of workers in a situation where personal sampling is not possible (see Note to 9.1.2.1 for an example of such a situation); to characterize the background level of HF and particulate fluorides in the workplace in order to give an indication of the efficiency of ventilation, or to provide information on the location and intensity of an emission source.

## 8.4 Selection of measurement conditions and measurement pattern

### 8.4.1 General

**8.4.1.1** Sampling shall be carried out in such a way as to cause the least possible interference with the worker and the normal performance of the job, and to provide samples that are representative of normal working conditions and that are compatible with the analytical method.

**8.4.1.2** The pattern of sampling shall take into consideration practical issues, such as the nature of the measurement task and the frequency and duration of particular work activities.

### 8.4.2 Screening measurements of variation of concentration in time and space

Screening measurements of variation of concentration in time and space are used to:

a) provide information on the likely pattern of concentration of chemical agents;

b) identify locations and periods of elevated exposure;

c) provide information on the location and intensity of emission sources;

d) estimate the effectiveness of ventilation or other technical measures.

### 8.4.3 Screening measurements of time-weighted average concentration and worst-case measurements

**8.4.3.1** Screening measurements of time-weighted average concentration are performed to obtain relatively crude quantitative information on the exposure level in order to decide whether an exposure problem exists at all and, if so, to appraise its possible seriousness. These measurements can also be used to determine if the exposure is well below or well above the limit value.

**8.4.3.2** Screening measurements of time-weighted average concentration are typically carried out in the initial stages of a survey to assess the effectiveness of control measures. Sampling may be carried out during representative work episodes to obtain clear information about the level and pattern of exposure, or worst-case measurements may be made.

NOTE Screening measurements of time-weighted average concentration made to identify clearly work episodes during which highest exposure occurs are typically referred to as “worst-case measurements”.

### 8.4.4 Measurements near an emission source

Measurements may be performed near an emission source to provide information on the location and intensity of the source. In association with other information, they can enable the elimination of a suspected source as a significant contributor to exposure.

### 8.4.5 Measurements for comparison with limit values and periodic measurements

#### 8.4.5.1 Measurements for comparison with limit values

**8.4.5.1.1** Measurements for comparison with limit values are performed to provide accurate and reliable information on, or enable the prediction of, the time-weighted average concentration of a specific chemical agent in the air that could be inhaled (see EN 482[10]).

**8.4.5.1.2** When making measurements for comparison with a short-term exposure limit, the sampling time shall be as close as possible to the reference period, which is typically 15 min.

**8.4.5.1.3** When making measurements for comparison with a long-term exposure limit, samples shall be collected for the entire working period, if possible, or during a number of representative work episodes (see 9.1.2.1 for the minimum sampling time).

NOTE The best estimate of long-term exposure is obtained by taking samples for the entire working period, but this is often not practicable (e.g. because of the possibility of overloading the filter).

#### 8.4.5.2 Periodic measurements

Periodic measurements are used to determine whether exposure conditions have changed since the measurements for comparison with limit values were performed, or whether control measures remain effective.

# 9 Sampling

## 9.1 Preliminary considerations

### 9.1.1 Selection and use of samplers

**9.1.1.1** Select samplers (7.1.1) designed to collect the inhalable fraction of airborne particles, as defined in ISO 7708, manufactured from a material that does not react with HF.

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.

**9.1.1.2** 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.

### 9.1.2 Sampling period

**9.1.2.1** Select a sampling period that is appropriate for the measurement task (see 8.4), but ensure that it is long enough to enable particulate fluorides and HF to be determined with acceptable uncertainty (see 3.5.8) at levels of industrial hygiene significance. For example, estimate the minimum sampling time, $t_{\text{min}}$, 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 a concentration of 0,1 times the limit value, using Equation (1):

$$t_{\text{min}} = \frac{m_{\text{lower}}}{q_V \times 0{,}1 \times \rho_{\text{LV}}} \tag{1}$$

where

$m_{\text{lower}}$ is the lower limit, in micrograms, of the analytical range;

$q_V$ is design flow rate, in litres per minute, of the sampler;

$\rho_{\text{LV}}$ is the limit value, in milligrams per cubic metre.

NOTE 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 (see 9.3.2.1).

**9.1.2.2** 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.

**9.1.2.3** 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 [20].

### 9.1.3 Temperature and pressure effects

#### 9.1.3.1 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, e.g. 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 (see 7.1.5), and measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see 9.4.1 and 9.4.2).

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

#### 9.1.3.2 Expression of results

Consider whether it is necessary to recalculate the concentration of HF and particulate fluorides 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 9.4.1 and 9.4.2) and use Equation (A.2) or (A.3) to apply the necessary correction.

NOTE The concentration of particulate fluorides and HF in air is generally stated for actual environmental conditions (temperature, pressure) at the workplace.

### 9.1.4 Sample handling

To minimize the risk of damage or contamination, only handle the pre-filters (7.1.2.1), HF sampling filters (7.1.2.2), and spacers (7.1.3) 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 (7.1.6.3).

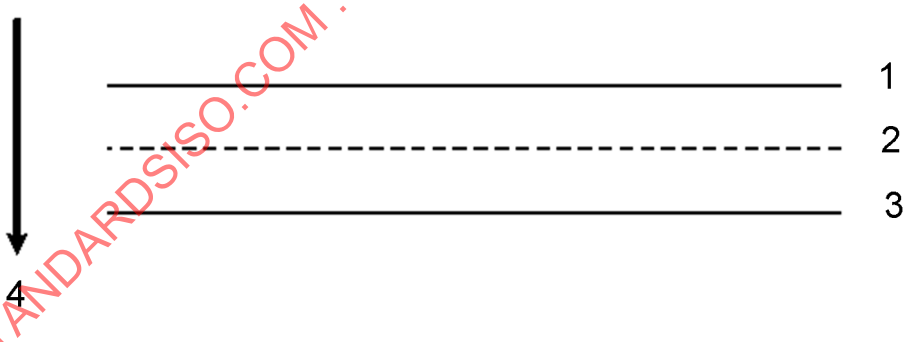
## 9.2 Preparation for sampling

### 9.2.1 Cleaning of samplers

Clean the samplers (7.1.1) before use, unless using disposable sampling cassettes. 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.

### 9.2.2 Loading the samplers with filters

Load each clean sampler (see 9.2.1), first with an HF sampling filter (7.1.2.2), then a spacer (7.1.3) and then a pre-filter (7.1.2.1). 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
3 HF sampling filter
4 direction of air flow through the sampler

**Figure 1 — Filter loading configuration**

### 9.2.3 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 (see 9.2.2) to a sampling pump (7.1.4) using flexible tubing (7.1.6.1), 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 (see 9.1.1.2). 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.

### 9.2.4 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.

## 9.3 Sampling position

### 9.3.1 Personal sampling

**9.3.1.1** Position the sampler in the worker's breathing zone as close to the mouth and nose as is reasonably practicable, e.g. fastened to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, e.g. to a belt (7.1.6.2) around the waist, or place it in a convenient pocket.

**9.3.1.2** 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.

### 9.3.2 Static sampling

**9.3.2.1** 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.

**9.3.2.2** 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.

## 9.4 Collection of samples

**9.4.1** 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. If appropriate (see 9.1.3), measure the atmospheric temperature and pressure at the start of the sampling period using the thermometer (7.1.6.4) and barometer (7.1.6.5), 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 can change and can require readjustment before sampling.

**9.4.2** 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 the sampling period. Measure the volumetric flow rate at the end of the sampling period using the flowmeter (7.1.5), and record the measured value. If appropriate (see 9.1.3), measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer (7.1.6.4) and barometer (7.1.6.5), and record the measured values.

**9.4.3** Carefully record the sample identity and all relevant sampling data (see Clause 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.

## 9.5 Transportation

### 9.5.1 Samplers with an internal filter cassette

For samplers with an internal filter cassette, remove the filter cassette from each sampler and fasten with its lid or transport clip.

### 9.5.2 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.

### 9.5.3 Transport of samples to the laboratory

**9.5.3.1** Transport the samples (9.5.1 and 9.5.2) 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.

**9.5.3.2** Ensure that the documentation which accompanies the samples is suitable for a "chain of custody" to be established (see, for example, ASTM D4840[8]).

# 10 Analysis

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

## 10.1 Preparation of test and calibration solutions

### 10.1.1 Selection of sample preparation method

Decide whether to use water (6.1) or eluent (6.4.10 or 6.4.12, depending on the analytical technique and separator column used) to prepare test solutions for determination of particulate fluorides and HF.

### 10.1.2 Preparation of test solutions

**10.1.2.1** Open each filter cassette or sampler (see 9.5) and transfer both filters into individual, labelled screw-cap vessels (7.2.3.2) or beakers (7.2.3.3) using clean tweezers (7.1.6.3), 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).

**10.1.2.2** Pipette 5,0 ml of water (6.1) into each screw-cap vessel (7.2.3.2) or beaker (7.2.3.3).

**10.1.2.3** Swirl gently to mix the contents, ensuring that the filter remains completely immersed. Sonicate for 15 min in an ultrasonic bath (7.2.5) and then allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally. (Ultrasonic treatment of the impregnated filter may be omitted, if desired.)

**10.1.2.4** Filter each sample solution through a PTFE filter (7.2.3.6), e.g. by using a disposable syringe (7.2.3.7), dispensing each filtrate into an individual, labelled, autosampler vial (7.2.3.8).

#### 10.1.3 Preparation of calibration solutions

Prepare a minimum of five calibration solutions to cover a concentration range, e.g. from 0,8 mg $l^{-1}$ to 8 mg $l^{-1}$ of fluoride. Accurately pipette appropriate volumes of fluoride working standard solution (6.5.2) into individual, labelled plastic one-mark volumetric flasks (7.2.3.1) or graduated centrifuge tubes (7.2.3.4), dilute to the mark with water (6.1), close and mix thoroughly. Prepare these calibration solutions fresh daily.

### 10.2 Instrumental analysis

#### 10.2.1 Setting up the instrument

**10.2.1.1** Set up the ion chromatograph in accordance with manufacturer's instructions.

**10.2.1.2** Install a sample loop that gives a suitable injection volume.

**10.2.1.3** Adjust the detector to measure to a suitable measuring range.

**10.2.1.4** Adjust the flow rate of the eluent (6.3, 6.4.10, 6.4.12) to a value that is compatible with the columns used.

**10.2.1.5** Adjust the flow rate of the regeneration solution to a suitable value.

#### 10.2.2 Analysis

**10.2.2.1** 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.

**10.2.2.2** Use the instrument's computer to generate a calibration function using a linear regression. Repeat the calibration if the coefficient of determination, $r^2$, is not greater than 0,999.

NOTE If $r^2$ <0,999, it can be possible to remove an erroneous calibration point and reprocess the data to obtain an acceptable calibration.

**10.2.2.3** 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 (10.2.2.2) to determine the fluoride concentrations in milligrams per litre.

**10.2.2.4** 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 detection limit, 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.

**10.2.2.5** Analyse reagent blank solutions and laboratory blank solutions as specified in 10.4.1, and quality control solutions as specified in 10.4.2.1. Use the results to monitor the performance of the method as specified in 10.4.2.2.

**10.2.2.6** 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, $f_{\text{dilution}}$.

For samples expected to have very high concentrations of fluoride, it may be necessary to dilute the test solutions before they are first analysed.

## 10.3 Estimation of detection and quantification limits

### 10.3.1 Estimation of the instrumental detection limit

**10.3.1.1** Estimate the instrumental detection limit under the working analytical conditions following the procedure described in 10.3.1.2 and 10.3.1.3 and repeat this exercise whenever the experimental conditions are changed significantly.

NOTE The instrumental detection limit is of use in identifying changes in instrument performance, but it is not a method detection limit (see Reference [23]). The instrumental detection limit is likely to be lower than the method detection limit, 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.

**10.3.1.2** Prepare a test solution with fluoride concentrations near the anticipated instrumental detection limits by diluting the working standard solution (6.5.2) by an appropriate factor.

**10.3.1.3** Make at least 10 ion chromatographic measurements on the test solution and calculate the instrumental detection limit as three times the sample standard deviation of the mean concentration value.

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

**10.3.2.1** Estimate the method detection limits and quantification limits under the working analytical conditions following the procedure described in 10.3.2.2 and 10.3.2.3 (which is based upon the approach described in Reference [24]), and repeat this exercise whenever the experimental conditions are changed significantly.

**10.3.2.2** 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 detection limits, e.g. 1 µg of fluoride, by spiking each filter with 0,01 ml of a solution prepared by diluting the working standard solution (6.5.2) by an appropriate factor. Prepare test solutions following the sample dissolution procedure used to prepare the sample test solutions (see 10.1.2).

**10.3.2.3** Make ion chromatographic measurements on the test solutions derived from each spiked filter (10.3.2.2) and calculate the method detection limit and the quantification limit 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 detection limit and the quantification limit for the determination of particulate fluoride and the results for the HF sampling filter give the method detection limit and the quantification limit for the determination of HF.

NOTE An alternative procedure for estimating the method detection limit involves the analysis of filter samples fortified with the analyte of interest at values spanning the predicted detection limit (see Reference [23]).

## 10.4 Quality control

### 10.4.1 Laboratory blanks

Carry reagent blanks (water and reagents) and media blanks (unspiked filters) throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Process reagent blanks according to a frequency of at least 1 in 20 samples or a minimum of one per batch.

### 10.4.2 Spiked samples and spiked duplicate samples

**10.4.2.1** 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 (6.5.2) 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.

**10.4.2.2** 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.

### 10.4.3 Certified reference materials

If available, suitable certified reference materials (CRMs)[1)] 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.

### 10.4.4 External quality assessment

If the laboratory carries out the analysis of fluoride in workplace air samples on a regular basis, it is recommended that it participate in a relevant external quality assessment scheme or proficiency testing scheme, if such a scheme exists and if it has access to it.

NOTE For information about existing proficiency testing schemes, refer, for example, to the EPTIS database (Reference [25]) or to a national accreditation organization.

## 10.5 Measurement uncertainty

It is strongly recommended that the laboratory estimate and report the uncertainty of its measurements in accordance with ISO/IEC Guide 98-3[4]. This entails constructing a cause and effect diagram (ISO 9004[3]) to identify the individual sources of random and systematic error in the overall sampling and analytical method. The standard uncertainties associated with these errors are then estimated, determined experimentally or both, and combined in what is referred to as an uncertainty budget. The combined standard uncertainty is ultimately multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of 2 is ordinarily recommended, giving a level of confidence of approximately 95 % in the calculated value.

NOTE 1 The application of cause and effect analysis to analytical methods is described in ISO/IEC Guide 98-3[4] and in References [26] and [27].

NOTE 2 See EN 13890[15] for guidance on including the uncertainty associated with sampling in the uncertainty budget.

NOTE 3 Terms that contribute to the random variability of an analytical method are generally accounted for in the measurement precision, which can be estimated from quality control data. Error associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the allowable drift before recalibration by $\sqrt{3}$ (see 10.2.2.4). Systematic errors of an analytical method include, for example, those associated with analytical recovery, preparation of working standard solutions, dilution of test solutions, etc.



1) CRMs are available from the European Commission and National Institute for Standards and Technology (NIST). This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the products supplied by these agencies.

## 11 Expression of results

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

$$\rho_{HF} = \frac{\left(\rho_{F,1} \times V_1 \times f_{dilution}\right) - \left(\rho_{F,0} \times V_0\right)}{V} \times f_{conversion} \quad (2)$$

$$\rho_{F} = \frac{\left(\rho_{F,1} \times V_1 \times f_{dilution}\right) - \left(\rho_{F,0} \times V_0\right)}{V} \quad (3)$$

where

$\rho_{HF}$ is the mass concentration, in milligrams per cubic metre, of HF, as fluoride, in the air sample;

$\rho_{F}$ is the mass concentration, in milligrams per cubic metre, of particulate fluorides, as fluoride, in the air sample;

$\rho_{F,0}$ is the mean concentration, in milligrams per litre, of fluoride in the blank test solutions;

$\rho_{F,1}$ 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).

## 12 Method performance

### 12.1 Sampling efficiency and sample storage

#### 12.1.1 HF

Laboratory testing with test atmospheres of HF has determined the sampling efficiency to be >95 % for HF in the range of 0,13 mg $m^{-3}$ to 5 mg $m^{-3}$ at humidities of up to 60 %. At a humidity of 80 %, the sampling efficiency decreases to 60 %. Recovery of HF was >95 % after two weeks sample storage. See Reference [20] for further information.

#### 12.1.2 Particulate fluorides

Laboratory testing with filters spiked with fluoride yielded a recovery of >95 % after four weeks sample storage. See Reference [20] for further information.

### 12.2 Quantification limit

The quantification limit of the method has been determined (see Reference [20]) to be 3,0 mg $l^{-1}$ for HF and 1,0 mg $l^{-1}$ 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 $m^{-3}$ for HF and 0,04 mg $m^{-3}$ for particulate fluorides.