INTERNATIONAL STANDARD

**ISO 21438-2**

First edition
2009-12-15

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

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

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

*Partie 2: Acides volatils, sauf acide fluorhydrique (acide chlorhydrique, acide bromhydrique et acide nitrique)*

Reference number
ISO 21438-2:2009(E)



ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

# Contents

Page

# 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.

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 21438-2 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 volatile inorganic acids. 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 volatile inorganic acids in use in industry, such as hydrochloric acid, hydrobromic acid and nitric acid, but excluding hydrofluoric acid. It is intended to be of benefit to: agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users of hydrochloric acid, hydrobromic acid and nitric acid and their workers, etc.

It has been assumed in the drafting of this part of ISO 21438 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 2: Volatile acids, except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid)

## 1 Scope

This part of ISO 21438 specifies a method for the determination of the time-weighted average mass concentration of hydrogen chloride (HCl) gas and hydrochloric acid mist, hydrogen bromide (HBr) vapour and hydrobromic acid mist and nitric acid ($HNO_3$) vapour and mist in workplace air by collection on an alkali-impregnated quartz fibre filter and analysis by ion chromatography.

For mist 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 analytical method is applicable to the determination of masses of 0,01 mg to 2,5 mg of HCl, HBr and $HNO_3$ per sample.

The range of concentrations of HCl, HBr and $HNO_3$ in air for which the measuring procedure is applicable is determined by the sampling method selected by the user. For a 240 l air sample, the working range is approximately 0,04 $mg \cdot m^{-3}$ to 10 $mg \cdot m^{-3}$ for HCl, HBr and $HNO_3$.

The procedure is intended to differentiate between the acids and their corresponding salts. If both are present in the air, particulate salts are trapped on a pre-filter. Co-sampled particulate matter trapped on the pre-filter and/or deposited on the walls of the sampler may be analysed, if desired.

Acids can react with co-sampled particulate matter on the pre-filter, causing interference with the measurement of the acid 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 648, *Laboratory glassware — Single-volume pipettes*

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*

ISO 8756, *Air quality — Handling of temperature, pressure and humidity data*

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

## 3 Terms and definitions

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

### 3.1 General definitions

**3.1.1**
**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 produced intentionally or not and whether placed on the market or not

[EN 1540:1998[1]]

**3.1.2**
**breathing zone**
⟨general definition⟩ space around the worker's face from where he or she takes his or her breath

**3.1.3**
**breathing zone**
⟨technical definition⟩ hemisphere (generally accepted to be 0,3 m in radius) extending in front of the human face, centred on the mid point of a line joining the ears, the base of the hemisphere being 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 1540:1998[1].

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

**3.1.5**
**measuring procedure**
procedure for sampling and analysing one or more chemical agents in the air and including storage and transportation of the sample

**3.1.6**
**operating time**
period during which a sampling pump can be operated at specified flow rate and back pressure without recharging or replacing the battery

[EN 1232:1997[2]]

**3.1.7**
**time-weighted average concentration**
**TWA concentration**
concentration of a chemical agent in the atmosphere, averaged over a reference period

NOTE More detailed discussion of TWA concentrations is available in Reference [3].

**3.1.8**
**limit value**
reference figure for concentration of a chemical agent in air

NOTE An example is the Threshold Limit Value® (TLV) for a given substance in workplace air, as established by the ACGIH[3].

**3.1.9**
**reference period**
specified period of time stated for the limit value of a specific chemical agent

NOTE Examples of limit values for different reference periods are short-term and long-term exposure limits, such as those established by the ACGIH[3].

**3.1.10**
**workplace**
defined area or areas in which the work activities are carried out

[EN 1540:1998[1]]

## 3.2 Particle size fraction definitions

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

[ISO 7708:1995]

**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 on other factors.

[ISO 7708:1995]

**3.2.3**
**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 particles concentration.

[ISO 7708:1995]

## 3.3 Sampling definitions

**3.3.1**
**personal sampler**
device attached to a person that samples air in the breathing zone

[EN 1540:1998[1]]

**3.3.2**
**personal sampling**
process of sampling carried out using a personal sampler

[EN 1540:1998[1]]

**3.3.3**
**sampling instrument**
**sampler**
〈for the purposes of this part of ISO 21438〉 device for collecting airborne particles

NOTE Instruments used to collect airborne particles are frequently referred to by a number of other terms, e.g. sampling heads, filter holders, filter cassettes.

**3.3.4**
**static sampling**
**area sampling**
process of air sampling carried out in a particular location

## 3.4 Analytical definitions

**3.4.1**
**blank solution**
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure as used for sample dissolution

**3.4.2**
**calibration blank solution**
calibration solution prepared without the addition of any working standard solution

NOTE The concentration of chloride, nitrate and bromide in the calibration blank solution is taken to be zero.

**3.4.3**
**calibration solution**
solution, prepared by dilution of a working standard solution, containing chloride, nitrate and bromide at concentrations that are suitable for use in calibration of an analytical instrument

**3.4.4**
**extraction solution**
solvent or solution used to solubilize the analyte(s) of interest

**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 as used for sampling, that does not leave the laboratory

**3.4.7**
**linear dynamic range**
range of concentrations over which the calibration curve for chloride, nitrate and bromide 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 as used for preparation of laboratory blank, field blank and sample solutions

**3.4.9**
**sample dissolution**
process of obtaining a solution containing chloride, nitrate and bromide from a sample, which might or might not involve complete dissolution of the sample

**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

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

NOTE 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.

**3.4.12**
**stock standard solution**
solution, used for preparation of the calibration solutions, containing chloride, nitrate and/or bromide at a certified concentration that is traceable to national standards

**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, e.g. dilution

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.

**3.4.14**
**working standard solution**
solution, prepared by dilution of the stock standard solution(s), that contains chloride, nitrate and bromide at concentrations that are better suited to preparation of calibration solutions than the concentration of chloride, nitrate and bromide in the stock standard solutions

## 3.5 Statistical terms

**3.5.1**
**analytical recovery**
ratio of the mass of analyte measured when a sample is analysed to the known mass of analyte in that sample, expressed as a percentage

**3.5.2**
**bias**
consistent deviation of the results of a measurement process from the true value of the air quality characteristic itself

**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 The coverage factor, $k$, is typically in the range from 2 to 3.

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

**3.5.4**
**combined standard uncertainty**
$u_c$
standard uncertainty of the result of 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]]

**3.5.5**
**expanded uncertainty**
quantity defining an interval about a result of a measurement, 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]]

**3.5.6**
**precision**
closeness of agreement of results obtained by applying the method several times under prescribed conditions

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

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

**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 can also be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information. ISO/IEC Guide 98-3[4] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

NOTE 3 Adapted from ISO/IEC Guide 99:2007[5].

## 4 Principle

**4.1** A known volume of air is drawn through a pre-filter and an alkali-impregnated quartz fibre sampling filter mounted in an inhalable sampler to collect HCl, HBr and $HNO_3$. The acids are collected on the sampling filter, while particulate salts of the acids are trapped on the pre-filter.

**4.2** The acids collected on the sampling filter are extracted with water or eluent (see 10.1.1), without heating, to solubilize the analytes of interest.

**4.3** Aliquots of the sample solution are subjected to ion chromatography in order to separate the extracted chloride, nitrate or bromide from other anions. Following this separation, the anions are measured using a conductivity or UV/visible detector.

**4.4** Analytical results are obtained by plotting the measured conductivity or absorbance as a function of concentration. The results can be used for assessment of occupational exposure to HCl, HBr and $HNO_3$ in air.

## 5 Requirement

The measuring procedure shall comply with any relevant international, European or national standard that specifies performance requirements for procedures for measuring chemical agents in workplace air (e.g. EN 482[6]).

## 6 Reagents

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

NOTE Chlorides and nitrates are found ubiquitously in the environment, and the presence of chloride and nitrate in reagents can lead to high blank values. It is therefore advisable to check the blank values of all chemicals before use.

**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 Reagents for impregnation of quartz fibre filters**.

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

**6.2.2 Sodium carbonate solution**, 2,5 mol·l$^{-1}$, for impregnation of 25 mm diameter quartz fibre filters.

Dissolve 26,5 g of $Na_2CO_3$ (6.2.1) in water. Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (7.2.2.1), dilute to the mark with water, stopper and mix thoroughly.

**6.2.3 Sodium carbonate solution**, 1 mol·l$^{-1}$, for impregnation of 37 mm diameter quartz fibre filters.

Dissolve 10,6 g of $Na_2CO_3$ (6.2.1) in water. Quantitatively transfer the solution into a 100 ml one-mark volumetric flask (7.2.2.1), dilute to the mark with water, stopper and mix thoroughly.

**6.3 Reagents for chemically suppressed ion chromatography**.

NOTE The sodium carbonate/sodium hydrogen carbonate eluent prescribed below is an example that can be used with separator columns for the analysis of chloride, bromide and nitrate by chemically suppressed ion chromatography. The column manufacturer's literature will give information on the composition of the eluent to be used with a specific column type.

**6.3.1 Sodium hydrogen carbonate ($NaHCO_3$)**, > 99,5 % mass fraction.

**6.3.2 Sodium carbonate/sodium hydrogen carbonate extraction and eluent stock solution**, 0,62 mol·l$^{-1}$ $Na_2CO_3$ and 0,069 mol·l$^{-1}$ $NaHCO_3$.

Dissolve 6,6 g of sodium carbonate (6.2.1) and 0,58 g of sodium hydrogen carbonate (6.3.1) in 25 ml of water (6.1) and swirl to mix. Quantitatively transfer the solution to a 100 ml one-mark volumetric flask (7.2.2.1), dilute to the mark with water, stopper and mix thoroughly.

**6.3.3 Sodium carbonate/sodium hydrogen carbonate extraction and eluent solution**, 0,003 1 mol·l$^{-1}$ $Na_2CO_3$ and 0,000 35 mol·l$^{-1}$ $NaHCO_3$.

Transfer 10 ml of sodium carbonate/sodium hydrogen carbonate stock solution (6.3.2) to a 2 l one-mark volumetric flask (7.2.2.1), dilute to the mark with water (6.1), stopper and mix thoroughly.

**6.3.4 Cartridge for eluent generation**.

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

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

NOTE The phthalic acid and borate/gluconate solutions prescribed below are two examples of eluents used in the analysis of chloride, bromide and nitrate using electronically suppressed ion chromatography. The column manufacturer's literature will give 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 ($LiOH·H_2O$)**, > 99,5 % mass fraction.

**6.4.5 Boric acid ($H_3BO_3$)**, > 99,8 % mass fraction.

**6.4.6 Gluconic acid solution**, mass fraction approximately 50 % 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 extraction and eluent stock solution**, 0,1 mol·l$^{-1}$ phthalic acid in a solvent mixture made up of 9 parts acetonitrile to 1 part 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 (7.2.2.1), dilute to the mark with water, stopper and mix thoroughly.

**6.4.10 Phthalic acid extraction solution and eluent**, e.g. 0,005 mol·l$^{-1}$ phthalic acid, pH 4,2.

Transfer an appropriate volume, e.g. 50 ml, of phthalic acid solution (6.4.8) to a 1 l beaker and add approximately 800 ml of water (6.1). Swirl to mix and adjust to pH 4,2 with lithium hydroxide solution (6.4.9). Transfer to a 1 l one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

**6.4.11 Borate/gluconate extraction and 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 gluconic acid solution (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 (7.2.2.1), dilute to the mark with water, stopper and mix thoroughly.

**6.4.12 Borate/gluconate extraction solution and eluent**.

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

**6.5 Chloride, bromide and nitrate standard solutions**.

**6.5.1 Chloride stock standard solution**.

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

**6.5.2 Bromide stock standard solution**.

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

**6.5.3 Nitrate stock standard solution**.

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

**6.5.4 Chloride, bromide and nitrate working standard solution**, 100 $mg \cdot l^{-1}$ of chloride, bromide and nitrate.

Accurately pipette appropriate volumes, e.g. 2 ml, of the chloride stock standard solution (6.5.1), bromide stock standard solution (6.5.2) and nitrate stock standard solution (6.5.3) into a 20 ml one-mark volumetric flask (7.2.2.1), 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 (see 7.1.2.1) and sampling filter (7.1.2.2) separated by a spacer (7.1.3), manufactured from a material that does not react with acids.

NOTE 1 If samplers have an internal filter cassette, this too has to be manufactured from a material that does not react with acids.

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, poly(vinyl chloride) (PVC), polyethylene, polypropylene and polycarbonate.

NOTE 3 CEN/TR 15230[7] gives examples of inhalable samplers with the potential to meet the requirements of EN 13205 that were available on the market up to 2004, including a list of 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**, with a collection efficiency of not less than 99,5 % for particles with a 0,3 µm diffusion diameter (see ISO 7708:1995, definition 2.2), manufactured from a material that does not react with HCl, HBr or $HNO_3$, for use as pre-filters to remove interfering particulate salts.

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

If the method prescribed in this part of ISO 21438 is to be used in conjunction with the method for determination of HF and particulate fluorides prescribed in ISO 21438-3, the pre-filter used shall be manufactured from a material that also does not react with HF.

**7.1.2.2 Filters**, quartz fibre, impregnated with sodium carbonate solution, for use as sampling filters for volatile inorganic acids, e.g. 25 mm diameter filters impregnated with 200 µl of 2,5 $mol \cdot l^{-1}$ sodium carbonate

solution (6.2.2) or 37 mm diameter filters impregnated with 500 µl of 1 $mol \cdot l^{-1}$ sodium carbonate solution (6.2.3) (see References [8] and [9]).

Refer to Clause B.2 for guidance on materials from which 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 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 shall 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 the flow rate designed in such a way that it can only be actuated with the aid of a tool (e.g. a 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.

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

EN 1232[2] and EN 12919[10] require that the performance of the pumps is 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[2] and/or EN 12919[10], appropriate action shall 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 Flow meter**, 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 flow meter shall be checked against a primary standard, i.e. a flow meter 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 flow meter was checked.

It is advisable that the flow meter 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 plastic or tipped with PTFE, for loading filters into, and unloading them from, samplers (see 9.2.2 and 10.1.2.1).

**7.1.6.4 Thermometer**, normally 0 °C to 50 °C, graduated in divisions of 1 °C or less, 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 the following.

NOTE It is preferable to use disposable plastic labware rather than glassware.

Chlorides, nitrates and, to a minor degree, bromides are found ubiquitously in the environment, and the presence of chlorides, in particular, can lead to elevated blanks. Check all disposable labware for chloride, nitrate and bromide contamination before use and clean all reusable laboratory apparatus thoroughly.

**7.2.1 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.

**7.2.2 Glassware**, made of borosilicate glass 3.3 complying with the requirements of ISO 3585, cleaned before use with water (6.1) (or with a suitable laboratory detergent, using a laboratory washing machine and afterwards rinsing thoroughly with water).

**7.2.2.1 One-mark volumetric flasks**, of suitable capacities between 10 ml and 2 l, complying with the requirements of ISO 1042.

**7.2.2.2 One-mark pipettes**, complying with the requirements of ISO 648.

**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 vessels**, disposable, of a suitable capacity, e.g. 20 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 Disposable filters**, PTFE, pore size 0,45 µm, for use in ion chromatography.

**7.2.3.6 Disposable syringes**, of a suitable capacity, e.g. 2 ml or 5 ml, with luer-lock connector, for use with disposable filters (7.2.3.5).

**7.2.3.7 Cation exchange resin cartridges**, suitable for removal of carbonate from test solutions to be analysed by electronically suppressed ion chromatography.

**7.2.3.8 Vacuum filtration system (or equivalent)**, for use with the cation exchange resin cartridges (7.2.3.7).

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

**7.2.4** **Piston-operated volumetric instruments**, with capacities of 10 µl to 5 ml, complying with the requirements of ISO 8655-1 and tested in accordance with ISO 8655-6; **piston-operated pipettes (pipettors)** complying with the requirements of ISO 8655-2 may be used as an alternative to one-mark pipettes (7.2.2.2) for the preparation of standard solutions and calibration solutions and for the dilution of samples.

**7.2.5** **Ultrasonic bath**, preferably with a timer, suitable for use in the ultrasonic extraction method for HCl, HBr and $HNO_3$ and for degassing the eluent solutions.

**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 comprised of inert materials, e.g. polyetheretherketone (PEEK).

**7.2.6.1** **Pump**, capable of delivering a constant flow within the range 0,1 $ml \cdot min^{-1}$ to 5 $ml \cdot min^{-1}$ 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 (see 7.2.6.5), as an alternative to use of a manually prepared eluent.

**7.2.6.3** **Sample injection system**, comprised of a low-dead-volume, non-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 (see 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 chloride, bromide and nitrate from other inorganic anions.

**7.2.6.5.2** **Separator column for electronically suppressed ion chromatography**, packed with silica or an organic polymer, suitable for resolving chloride, bromide and nitrate from other inorganic anions.

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

**7.2.6.7** **Conductivity detector**, flow-through, low-volume, with a non-metallic flow path.

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

**7.2.6.8** **UV/visible detector**, flow-through, low-volume.

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

**7.2.6.9** **Recorder, integrator** or **computer**, compatible with the detector output, capable of recording the 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 (see 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[6], EN 689[11], ASTM E1370[12]) 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 HCl, HBr and $HNO_3$ shall normally be determined by personal sampling, since the concentration of HCl, HBr and $HNO_3$ 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 in 9.1.2.1 for an example of such a situation); to characterize the background level of HCl, HBr and $HNO_3$ 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/or space

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

— provide information on the likely pattern of concentration of chemical agents;

— identify locations and periods of elevated exposure;

— provide information on the location and intensity of emission sources;

— 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 clearly identify 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 allow 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 allow the prediction of, the time-weighted average concentration of a specific chemical agent in the air that could be inhaled (see EN 482[6]).

**8.4.5.1.2** For 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** For 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).

The best estimate of long-term exposure is obtained by taking samples for the entire working period, but this is often not applicable, e.g. because of the limited sampling capacity of the impregnated filter (see 12.3). In such instances, consecutive sampling may be used. See Reference [12] for further guidance.

##### 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.

If possible, the samplers selected should be manufactured from conducting material, since samplers manufactured from non-conducting material have electrostatic properties that can influence the representative nature of the sampling.

**9.1.1.2** Use the samplers at their design flow rate and in accordance with the instructions provided by the manufacturer. See Reference [7] 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 HCl, HBr or $HNO_3$ in the air to be determined with acceptable uncertainty (see 3.5.8) at levels of industrial hygiene significance. For example, estimate the minimum sampling time required to ensure that the amount collected is above the lower limit of the working range of the analytical method when HCl, HBr or $HNO_3$ is 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 the following equation:

$$t_{\text{min}} = \frac{m_{\text{lower}}}{q_{\text{V}}\, k\, \rho_{\text{LV}}}$$

where

$t_{\text{min}}$ is the minimum sampling time, in minutes;

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

$q_{\text{V}}$ is the 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);

$\rho_{\text{LV}}$ 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.

**9.1.2.2** When high concentrations of HCl, HBr or $HNO_3$ are anticipated, select a sampling period that is not so long as to risk exceeding the maximum sampling capacity of the sampling filter (see 12.3).

**9.1.2.3** 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.

### 9.1.3 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 if the indicated volumetric flow rate of the flow meter (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 flow meter 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 flow meter 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 Clause A.1 for a constant pressure drop, variable area, flow meter.

#### 9.1.3.2 Expression of results

Consider whether it is necessary to recalculate the concentration of HCl, HBr and $HNO_3$ in the air to reference conditions (see ISO 8756). 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 the equation given in Clause A.2 to apply the necessary correction.

NOTE The concentration of HCl, HBr or $HNO_3$ in air is generally stated for the actual environmental conditions (temperature and pressure) at the workplace.

### 9.1.4 Sample handling

To minimize the risk of damage or contamination, only handle pre-filters (7.1.2.1), sampling filters (7.1.2.2) and spacers (7.1.3) in a clean area where the concentration of HCl, HBr and $HNO_3$ in the air is minimal and only handle using tweezers (7.1.6.3).

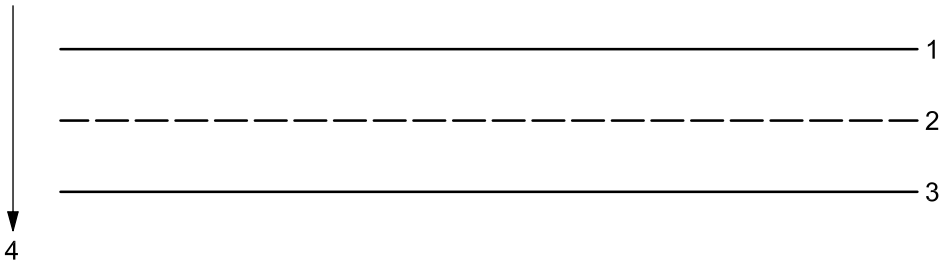
## 9.2 Preparation for sampling

### 9.2.1 Cleaning of samplers

Clean the samplers (7.1.1) before use, unless using disposable sampling cassettes. Disassemble the samplers, soak in detergent solution, rinse thoroughly with water, wipe with absorbent tissue and allow to dry before reassembly. Alternatively, use a laboratory washing machine.

### 9.2.2 Loading the aerosol samplers with filters

Load each clean sampler (see 9.2.1), first with a sampling filter (7.1.2.2), then with a pre-filter (7.1.2.1), separating the filters with a spacer (7.1.3). 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 sampling 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 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 concentration of HCl, HBr and $HNO_3$ is 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 flow meter (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 field blanks one unused loaded sampler from each batch of ten 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 work process is likely to result in a significant difference between the actual exposure of the worker and the concentration of HCl, HBr or $HNO_3$ 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 HCl, HBr or $HNO_3$ in the workplace, select a sampling position that is sufficiently remote from the work processes, such that results are not directly affected by HCl, HBr or $HNO_3$ 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 could change and it might need to be re-adjusted before sampling begins.

**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 and/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 flow meter (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 of the sampling period in minutes.

## 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 (see 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 assure 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[14]).

**9.5.3.3** After sampling, store the internal filter cassette or sampler for at least 4 days for equilibration before opening for analysis[9].

## 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 the extraction solution

Decide whether to use water (6.1) or eluent (6.3.3, 6.4.10 or 6.4.12, depending on the analytical technique and separator column used) to prepare test solutions for determination of HCl, HBr or $HNO_3$.

#### 10.1.2 Preparation of test solutions

**10.1.2.1** Open the filter cassettes or samplers (see 9.5) and transfer each sampling filter into an individual, labelled, screw-cap vessel (7.2.3.2) or beaker (7.2.3.3), using clean tweezers (7.1.6.3). Follow the same procedure for the blank filters (see 9.2.4).

If analysis of co-sampled particulate matter is desired, retain the pre-filter and sampler.

**10.1.2.2** Accurately pipette a suitable volume, e.g. 10,0 ml, of extraction solution (see 10.1.1) into each beaker or screw-cap vessel.

**10.1.2.3** Swirl gently to mix the contents, ensuring that the filter remains completely immersed. Treatment for 15 min in an ultrasonic bath (7.2.5) is recommended.

**10.1.2.4** Allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally. If ultrasonication is used as recommended in 10.1.2.3, this step may be omitted.

**10.1.2.5** For preparation of test solutions for analysis by chemically suppressed ion chromatography, filter a portion of each sample solution through a PTFE filter (7.2.3.5), e.g. by using a disposable syringe (7.2.3.6), dispensing each filtrate into an individual, labelled autosampler vial (7.2.3.9).

**10.1.2.6** For preparation of test solutions for analysis by electronically suppressed ion chromatography, pass a portion of each sample solution, e.g. 2 ml, through a cation exchange resin cartridge (7.2.3.7) to remove carbonate.

### 10.1.3 Preparation of calibration solutions

**10.1.3.1** Prepare a minimum of five calibration solutions to cover a suitable concentration range, e.g. from 0,4 $mg \cdot l^{-1}$ to 4 $mg \cdot l^{-1}$ of chloride, bromide and nitrate. Accurately pipette appropriate volumes of chloride, nitrate and bromide working standard solution (6.5.4) into individual, labelled, 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.

NOTE If required, the calibration solutions can be matrix-matched prior to making up to volume, e.g. by addition of an appropriate volume of extraction and eluent stock solution.

**10.1.3.2** For electronically suppressed ion chromatography calibration, pass a portion of each solution, e.g. 2 ml, through a cation exchange resin cartridge (7.2.3.7) to remove carbonate.

## 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 (6.3.3, 6.4.10 or 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 (see 10.1.3) into the ion chromatography system in order of increasing concentration and measure the chloride, bromide and nitrate peaks for each calibration solution in the 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 $> 0{,}999$.

NOTE If $r^2 < 0{,}999$, it might 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 (see 10.1.2,) into the ion chromatography system and make measurements for each solution. Use the stored calibration function (see 10.2.2.2) to determine the chloride, bromide and nitrate concentrations in $mg \cdot l^{-1}$.

**10.2.2.4** Analyse the calibration blank solution and a mid-range calibration solution after the initial calibration and then after every ten test solutions. If the measured concentration of chloride, bromide or nitrate in the continuing calibration blank is above the method detection limit, as determined in 10.3.2, or if the measured concentration of chloride, bromide or nitrate in the continuing calibration verification 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 10.4.1.1 and quality control solutions as specified in 10.4.2.1, and use the results to monitor the performance of the method as specified in 10.4.1.2 and 10.4.2.2.

**10.2.2.6** If the concentration of chloride, bromide or nitrate is 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 (see 10.1.1) when making dilutions, so that the diluted test solutions and the calibration solutions are matrix-matched, and record the dilution factor.

NOTE For samples expected to have very high concentrations of chloride, bromide or nitrate, it might 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 [15]). 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 chloride, nitrate and bromide concentrations near the anticipated instrumental detection limits by diluting the working standard solution (6.5.4) by an appropriate factor.

**10.3.1.3** Make at least ten 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 limit and quantification limit

**10.3.2.1** Estimate the method detection limit and quantification limit 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 [16]), and repeat this exercise whenever the experimental conditions are changed significantly.

**10.3.2.2** Fortify at least ten sampling filters (7.1.2.2) with chloride, nitrate and bromide near the anticipated method detection limits, e.g. 1 µg of chloride, nitrate or bromide, by spiking each filter with 0,01 ml of a solution prepared by diluting the working standard solution (6.5.4) 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 (see 10.3.2.2) and calculate the method detection limit and the quantification limit as three times and ten times the sample standard deviation of the mean concentration value, respectively.

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 [15]).

## 10.4 Quality control

### 10.4.1 Reagent blanks and laboratory blanks

**10.4.1.1** Carry reagent blanks (see 3.4.8) and laboratory blanks (see 3.4.6) 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.

**10.4.1.2** 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.

### 10.4.2 Quality control solutions

**10.4.2.1** Carry spiked samples and spiked duplicate samples through the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of filters to which known amounts of chloride, bromide and nitrate have been added. (This can be accomplished by spiking with known volumes of chloride, bromide and nitrate working standard solution at amounts within the linear dynamic range of the instrument. The chloride, bromide and nitrate working standard solution used shall be prepared from chloride, bromide and nitrate stock standard solutions from a different source from that used for preparing the calibration solutions.) Process these quality control samples at a frequency of at least one per 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 percent recoveries and of the relative percent 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 re-analyse the samples if necessary. See ASTM E882[17] for general guidance on the use of quality control charts.

### 10.4.3 Certified reference materials (CRMs)

If available, suitable CRMs for HCl, HBr or $HNO_3$ shall be analysed prior to routine use of the method to establish that the percent recovery relative to the certified value is satisfactory.

### 10.4.4 External quality assessment

If laboratories carry out HCl, HBr or $HNO_3$ in air analysis on a regular basis, it is recommended that they participate in a relevant external quality assessment scheme or proficiency testing scheme, if such a scheme exists and they have access to it.

NOTE For information about existing proficiency testing schemes, refer, for example, to the database EPTIS (European Information System on Proficiency Testing Schemes, www.eptis.bam.de) or a national accreditation organization.

## 10.5 Measurement uncertainty

It is recommended that laboratories estimate and report the uncertainty of their measurements in accordance with ISO/IEC Guide 98-3[4]. The first step is to construct a cause-and-effect diagram 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 2 is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 References [18] and [19] 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 (see 10.2.2.4) by $\sqrt{3}$.

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

## 11 Expression of results

Calculate the mass concentration of HCl, HBr or $HNO_3$ in the air samples at ambient conditions, $\rho$[acid], in milligrams per cubic metre, using the equation:

$$\rho[\text{acid}] = \frac{\left(\rho[\text{anion}]_1 V_1 f_\text{d}\right) - \left(\rho[\text{anion}]_0 V_0\right)}{V} f_\text{c}$$

where

$\rho[\text{anion}]_0$ is the mean concentration of chloride, bromide and nitrate in the field blank test solutions, in milligrams per litre;

$\rho[\text{anion}]_1$ is the concentration of chloride, bromide and nitrate in the sample test solution, in milligrams per litre;

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

$V_0$ is the volume, in millilitres, of the field blank test solutions;

$V_1$ is the volume, in millilitres, of the sample test solution;

$f_\text{d}$ is the dilution factor ($f_\text{d}$ = 1 in the absence of dilution);

$f_\text{c}$ is a factor to convert from anion to acid concentration ($f_\text{c}$ = 1,028 4 for chloride, $f_\text{c}$ = 1,012 6 for bromide and $f_\text{c}$ = 1,016 3 for nitrate).

## 12 Method performance

### 12.1 Sampling efficiency and sample storage

Laboratory testing[20] with test atmospheres of HCl, HBr and $HNO_3$ vapour has determined the sampling efficiency to be $> 95$ % for HCl in the range 0,1 mg·m$^{-3}$ to 10 mg·m$^{-3}$, HBr in the range 0,5 mg·m$^{-3}$ to 10 mg·m$^{-3}$ and $HNO_3$ in the range 0,1 mg·m$^{-3}$ to 10 mg·m$^{-3}$. Recovery of HCl, HBr or $HNO_3$ was found to be $> 95$ % after four weeks sample storage. See Reference [9] for further information.

NOTE The sampling efficiency of the method is diminished if the pre-filter retains some of the sampled acid. Laboratory testing[20] has shown that small amounts of $HNO_3$ can be retained on certain types of pre-filter and this affects the quantification limit of the method if not corrected.

### 12.2 Quantification limits

The quantification limits of the method have been determined[9] to be 1 mg·l$^{-1}$ for chloride, bromide and nitrate. For a sample solution volume of 10 ml and an air sample volume of 240 l, this is equivalent to 0,04 mg·m$^{-3}$ for all three acids.

### 12.3 Upper limits of the working range

The upper limit of the working range of the method is governed by the maximum permissible loading of the sampling filters. It has been demonstrated that no breakthrough occurs at sample loadings of up to at least 0,4 mmol of acid, e.g. approximately 15 mg of HCl or 30 mg of $HNO_3$.

## 12.4 Bias and precision

### 12.4.1 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[9] to be in the range 96 % to 100 % for hydrochloric and nitric acid.

### 12.4.2 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, has been found[9] to be in the range 0,4 % to 1,7 % for HCl and 1,1 % to 1,9 % for $HNO_3$.

## 12.5 Uncertainty of sampling and analysis method

The expanded uncertainty of the method, using a coverage factor of 2, has been estimated[9] to be < 12 % for HCl and HBr and < 14 % for $HNO_3$.

## 12.6 Interferences

**12.6.1** The ubiquitous presence of chlorides and nitrates leads to blank values being produced by the reagents and equipment used in the method (i.e. the chemicals and glassware). Therefore the blank values of all chemicals and equipment have to be carefully checked.

**12.6.2** An interlaboratory evaluation of the method was carried out at a test gas facility using different sampler and filter types. Samples were collected at a concentration of 2 $mg \cdot m^{-3}$ for HCl and $HNO_3$ under typical environmental conditions (temperature ~ 20 °C, humidity ~ 50 %). For estimation of possible interferences, the pre-filter was pre-loaded with a number of potential interferents. It was found that iron, zinc oxide and welding fumes can react with the acid gases and lead to significant sample loss. Iron oxide was found not to interfere with the determination.

**12.6.3** If particulate salts containing chloride, bromide and nitrate are collected on the pre-filter together with a stronger acid such as sulfuric acid, this will lead to displacement of chloride, bromide and nitrate and a positive interference on acid results.

# 13 Test report

## 13.1 Test record

A comprehensive record of the test performed shall be maintained, including the following information:

a) a statement to indicate the confidentiality of the information supplied, if appropriate;

b) 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 another personal identifier) or the location at which the general occupational environment was sampled (for a static sample), a brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;

c) a reference to this part of ISO 21438;

d) the makes, types and diameters of the filters used;

e) the make and type of sampler used;

f) the make and type of sampling pump used, and its identification;

g) the make and type of flow meter used, the primary standard against which the calibration of the flow meter was checked, the range of flow rates over which the calibration of the flow meter was checked, and the atmospheric temperature and pressure at which the calibration of the flow meter was checked, if appropriate (see 9.1.3);

h) the time at the start and at the end of the sampling period, and the duration of the sampling period, in minutes;

i) the mean flow rate during the sampling period, in litres per minute;

j) the mean atmospheric temperature and pressure during the sampling period, if appropriate (see 9.1.3);

k) the volume of air sampled, in litres, at ambient conditions;

l) the name of the person who collected the sample;

m) the time-weighted average mass concentration of HCl, HBr or $HNO_3$ found in the air sample (in $mg \cdot m^{-3}$), at ambient temperature and pressure, or, if appropriate, adjusted to reference conditions;

n) the analytical variables used to calculate the result, including the concentrations of chloride, bromide and nitrate 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 may contain the analytical result in micrograms of HCl, HBr or $HNO_3$ per filter sample.

o) the type(s) of instrument(s) used for sample preparation and analysis, and unique identifiers(s);

p) the estimated instrumental detection limits, method detection limits and quantification limits 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;

q) any operation not specified in this part of ISO 21438 or regarded as optional;

r) the name of the analyst(s) [or other unique identifier(s)];

s) the date of the analysis;

t) any inadvertent deviations, unusual occurrences or other notable observations.

## 13.2 Laboratory report

The laboratory report shall contain all information required by the end user, regulatory authorities and accreditation organizations.

# Annex A
(informative)

# Temperature and pressure correction

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

Bubble flow meters are preferred for measuring the volumetric flow rate because the readings they give are independent of temperature and pressure. For other flow meters, it might be necessary to apply a correction to the indicated volumetric flow rate if the temperature and pressure at the time of measurement are different from when the calibration of the flow meter was checked.

A typical example of the need for a temperature and pressure correction is when a constant pressure drop, variable area, flow meter is used to measure the volumetric flow rate. In this instance, use the following equation to calculate a corrected air sample volume:

$$V_{\text{corr}} = q_{\text{V}}\, t \sqrt{\frac{p_1\, T_2}{p_2\, T_1}}$$

where

$V_{\text{corr}}$ is the corrected volume, in litres;

$q_{\text{V}}$ 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 flow meter;

$p_2$ is the mean atmospheric pressure, in kilopascals, during the sampling period;

$T_1$ is the temperature, in kelvins, during calibration of the sampling pump flow meter;

$T_2$ is the mean temperature, in kelvins, 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 increase in 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 flow meter can also require a correction for variation in pressure and temperature. Follow the manufacturer's instructions for such corrections.

## A.2 Recalculation of concentrations of HCl, HBr and $HNO_3$ in air to reference conditions

If necessary (see 9.1.3.2), recalculate the concentrations of HCl, HBr or $HNO_3$ in the air to reference conditions (e.g. 293 K and 101,3 kPa), using the following equation:

$$\rho[\text{acid}]_{\text{corr}} = \rho[\text{acid}] \frac{101{,}3 \times T_2}{p_2 \times 293}$$

where

$\rho[\text{acid}]_{\text{corr}}$ is the corrected concentration of HCl, HBr or $HNO_3$ in the air sample, in milligrams per cubic metre, at reference conditions;

$\rho[\text{acid}]$ is the concentration of HCl, HBr or $HNO_3$ in the air sample, in milligrams per cubic metre, at ambient conditions;

$T_2$ is the mean temperature, in kelvins, during the sampling period;

$p_2$ is the mean atmospheric pressure, in kilopascals, during the sampling period;

293 is the reference temperature (20 °C), in kelvins;

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

# Annex B
(normative)

# Filter materials

## B.1 Pre-filters

The purpose of the pre-filters is to trap particulate salts and separate them from HCl, HBr and $HNO_3$. However, in many workplaces the volatile acids are 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, the volatile acids vaporize and are subsequently collected on the sampling filters. The pre-filters are normally discarded after sampling unless the collected particulate salts are to be analysed for a purpose not covered by this part of ISO 21438, e.g. to determine zinc chloride and ammonium chloride in a hot-dip-galvanizing plant in which an HCl pickling tank is in use.

Chlorides, nitrates and, to a lesser extent, bromides, are found ubiquitously in the environment, and contamination of the pre-filters can lead to high blanks, especially for chloride. If the pre-filters are to be analysed, it is therefore advisable to check that the level and variability of chloride, bromide and nitrate in the filters are low before use.

Even if the pre-filters are discarded after sampling, it is still important that they contain low levels of chloride, bromide and nitrate. This is because, if there is a stronger acid, such as sulfuric acid, present in the sampled air, HCl, HBr and $HNO_3$ can be displaced from chlorides, bromides and nitrates present on the pre-filters and subsequently be collected on the sampling filters, causing a positive interference (see 12.6.3).

PTFE and PVC membrane filters, of pore size 5 µm and below, and quartz fibre filters are generally suitable for use as pre-filters, but a laboratory study[21] has shown that the level and variability of blanks can differ significantly depending on the supplier and the individual filter batch.

## B.2 Sampling filters

Filters made from many polymeric materials cannot be used to prepare sampling filters because they have hydrophobic properties that make them unsuitable for impregnation with sodium carbonate solution. The use of quartz fibre filters is recommended, but a laboratory study[21] has shown that the level and variability of blanks can differ significantly depending on the supplier and the individual filter batch.

As already mentioned, chlorides, nitrates and, to a lesser extent, bromides, are found ubiquitously in the environment, and contamination of alkali-impregnated quartz fibre filters can lead to high blank values, in particular for chloride. It is therefore advisable to check that the level and variability of chloride, bromide and nitrate on filters are low before impregnation with sodium carbonate solution and to verify that each batch of sampling filters prepared is fit for use by determining the quantification limit following the procedure prescribed in 10.3.2.

# Bibliography


[1] EN 1540:1998, *Workplace atmospheres — Terminology*

[2] EN 1232:1997, *Workplace atmospheres — Pumps for personal sampling of chemical agents — Requirements and test methods*

[3] *Documentation of the Threshold Limit Values and Biological Exposure Indices*, American Conference of Government Industrial Hygienists (ACGIH), Cincinnati, OH, USA, updated annually, available (at time of publication of this part of ISO 21438) at www.acgih.org

[4] ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

[5] ISO/IEC Guide 99:2007, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

[6] EN 482, *Workplace atmospheres — General requirements for the performance of procedures for the measurement of chemical agents*

[7] CEN/TR 15230, *Workplace atmospheres — Guidance for sampling of inhalable, thoracic and respirable aerosol fractions*

[8] Institut National de Recherche et de Sécurité (INRS), Base de données MétroPol, Fiche 009: *Anions minéraux*, available (at time of publication of this part of ISO 21438) at www.inrs.fr/metropol

[9] BREUER, D., and GUSBETH, K., *Anorganische Säuren, flüchtig: Bromwasserstoff, Chlorwasserstoff, Salpetersäure* (Inorganic acids, volatile: hydrogen bromide, hydrogen chloride, nitric acid), Berufsgenossenschaftliche Institut für Arbeitsschutz (BGIA), publication reference No. 6172, Erich Schmidt Verlag, Bielefeld, Germany, 2007, ISBN 3 503 020853

[10] EN 12919, *Workplace atmospheres — Pumps for the sampling of chemical agents with a volume flow rate of over 5 l/min — Requirements and test methods*

[11] EN 689:1995, *Workplace atmospheres — Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy*

[12] ASTM E1370, *Standard Guide for Air Sampling Strategies for Worker and Workplace Protection*

[13] ISO 21438-3, *Workplace atmospheres — Determination of inorganic acids by ion chromatography — Part 3: Hydrofluoric acid and particulate fluorides*

[14] ASTM D4840, *Standard Guide for Sample Chain-of-Custody Procedures*

[15] KENNEDY, E.R., FISCHBACH, T.J., SONG, R., ELLER, P.M., SHULMAN, S., *Guidelines for air sampling and analytical method development and evaluation*, U.S. Dept. of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH, USA, 1995, 104 pp. http://www.cdc.gov/niosh

[16] CURRIE, L.A., Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC Recommendations 1995), *Pure Appl. Chem.*, 1995, **67**, pp. 1699-1723

[17] ASTM E882, *Standard Guide for Accountability and Quality Control in the Chemical Analysis Laboratory*

[18] ELLISON, S.L.R., and BARWICK, V.J., Estimating measurement uncertainty: Reconciliation using a cause and effect approach, *Accred. Qual. Assur.*, 1998, **3**, pp. 101-105

[19] ELLISON, S.L.R., and BARWICK, V.J., Using validation data for ISO measurement uncertainty investigation: Part 1 — Principles of an approach using cause and effect analysis, *Analyst*, 1998, **123**, pp. 1387-1392

[20] BREUER, D., and HOWE, A.M., Performance of methods for measurement of exposure to inorganic acids in workplace air, *J. Environ. Monit.*, 2006, **8**, pp. 120-126

[21] BREUER, D., DEMANGE, M., and HOWE, A.M., *Evaluation of sampling methods used in the measurement of exposure to hydrochloric acid (HCL) and nitric acid ($HNO_3$) in workplace air* (in press)

**ICS 13.040.30**

Price based on 29 pages