International
Standard

ISO 21438-2

Second edition
2024-01

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 21438-2:2024(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Foreword

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

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

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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

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

This second edition cancels and replaces the first edition (ISO 21438-2:2009), which has been technically revised.

The main changes are as follows:

- terms, definitions and references have been updated;
- information on sample preparation and analytical methodology has been updated.

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

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

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 document has been published in order to make available a method for making valid exposure measurements for volatile inorganic acids in use in the industry, such as hydrochloric acid, hydrobromic acid and nitric acid, but excluding hydrofluoric acid. This document 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.

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

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 either trapped on the pre-filter or deposited on the walls of the sampler, or both, can 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.

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

2 Normative references

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

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3585, *Borosilicate glass 3.3 — Properties*

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

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

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

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

ISO 8655-6, *Piston-operated volumetric apparatus — Part 6: Gravimetric reference measurement procedure for the determination of volume*

ISO 18158, *Workplace air — Terminology*

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

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

EN 13205, *Workplace exposure — Assessment of sampler performance for measurement of airborne particle concentrations*

3 Terms and definitions

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

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

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

3.1
blank solution
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for *sample dissolution* (3.5)

3.2
calibration blank solution
calibration solution (3.3) prepared without the addition of any *working standard solution* (3.9)

Note 1 to entry: The concentration of chloride, bromide and nitrate in the calibration blank solution is taken to be zero.

3.3
calibration solution
solution prepared by dilution of the *working standard solution* (3.9), containing chloride, bromide and nitrate at concentrations that are suitable for use in calibration of the analytical instrument

3.4
extraction solution
solvent or solution used to solubilise the analyte(s) of interest

3.5
sample dissolution
process of obtaining a solution containing chloride, bromide and nitrate from a sample, which does or does not involve complete dissolution of the sample

3.6
sample solution
solution prepared from a sample by the process of *sample dissolution* (3.5)

Note 1 to entry: A sample solution can require further operations, for example, dilution, in order to produce a *test solution* (3.8) that is ready for analysis.

3.7
stock standard solution
solution, used for preparation of the *calibration solutions* (3.3), containing chloride, bromide and/or nitrate at a certified concentration that is traceable to national standards

3.8
test solution
blank solution (3.1) or *sample solution* (3.6) that has been subjected to all operations required to bring it into a state in which it is ready for analysis, e.g. dilution, filtered

Note 1 to entry: The blank test solution is the blank solution and the sample test solution is the sample solution if these solutions are not subjected to any further operations before analysis.

3.9
working standard solution
solution, prepared by dilution of the *stock standard solution(s)* (3.7), that contains chloride, bromide and nitrate at concentrations that are better suited to the preparation of *calibration solutions* (3.3) than the concentrations of chloride, bromide and nitrate in the stock standard solution(s)

4 Principle

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.

The acids collected on the sampling filter are extracted with water or eluent (see 10.1.2), without heating, to solubilize the analytes of interest.

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.

Analytical results are obtained by plotting the measured signal as a function of concentration. They can be used for assessing the occupational exposure to HCl, HBr and HNO_3 in the air.

5 Requirement

The measuring procedure shall comply with the performance requirements for procedures for measuring chemical agents in workplace air given in ISO 20581.

6 Reagents

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

NOTE 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 of grade 1, in accordance with the requirements of ISO 3696.

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

6.2 Sodium carbonate (Na_2CO_3), anhydrous, mass fraction greater than 99,9 %.

6.3 Sodium carbonate solution, 1 mol/l, for impregnation of 37 mm diameter quartz fibre filters.

Dissolve 10,6 g of Na_2CO_3 (6.2) in water. Quantitatively transfer the solution into a 100 ml one-mark volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

6.4 Sodium bicarbonate ($NaHCO_3$), anhydrous, mass fraction greater than 99,9 %.

6.5 Sodium carbonate/sodium bicarbonate extraction and eluent stock solution.

Create a stock solution for the extraction and eluent solution. The stock solution shall be appropriate to the used application.

6.6 Sodium carbonate/sodium bicarbonate extraction and eluent solution.

The concentration of the extraction and eluent solution are typically matched, but this can be modified according to the laboratory procedure.

NOTE An alkaline solution (potassium hydroxide or sodium hydroxide) can be used in place of the buffer solution according to modifications to the method, but the resulting solution will require adjustment before analysis.

6.7 Chloride, bromide and nitrate standard solutions.

6.7.1 Chloride, bromide and nitrate stock solutions.

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

6.7.2 Chloride, bromide and nitrate calibration solutions.

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

6.8 Chloride, bromide and nitrate check-standard.

Use a certified reference material (CRM) as described in 10.4.3 with a certificate of its concentration, for example, 200 mg/l for chloride, 400 mg/l for bromide and 400 mg/l for nitrate, traceable to national standards. Observe the manufacturer's expiry date or recommended shelf-life.

6.9 Chloride, bromide and nitrate check-standard working solution.

The check-standard working solution should be in the middle of the calibration range. Pipette a proper volume of check-standard (6.8) to create a check-standard working solution with the eluent (6.6). Prepare this solution fresh for every calibration. If necessary, create a check-standard working solution for chloride, bromide and nitrate separately.

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 and sampling filter separated by a spacer, 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, polyvinyl chloride (PVC), polyethylene, polypropylene and polycarbonate.

NOTE 3 CEN/TR 15230[9] 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).

Hydrogen chloride (HCl) gas and hydrochloric acid mist, hydrogen bromide (HBr) vapour and hydrobromic acid mist and nitric acid (HNO_3) vapour and mist are strong acids. Therefore, correct selection of the filter used for sample collection is of paramount importance. Also, some filters, for example, glass fibre filters, can contain metals, for example, barium, that react with acids to produce insoluble salts.

Chloride, bromide and nitrate are found ubiquitously in the environment and the presence of chloride, bromide and nitrate in filter materials can lead to high blank values. It is therefore essential to check the blank values of each batch of filters used.

7.1.2.1 Pre-filters, of a diameter suitable for use with the samplers (7.1.1), with a collection efficiency ≥99 % for particles with a 0,3 µm diffusion diameter and manufactured from a material that does not react with HCl, HBr or HNO_3, for use as pre-filters to remove interfering particulate salts and also is compatible with the sample preparation and analysis method.

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

7.1.2.2 Sampling filters, such as 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/l sodium carbonate solution or 37 mm diameter filters impregnated with 500 µl of 1 mol/l sodium carbonate solution (6.3) (see References [10] and [11]).

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, according to ISO 13137[1] should be used.

If the sampling pump is used outside the range of conditions specified in ISO 13137[1] appropriate action should be taken to ensure that the performance requirements are met. For instance, at sub-zero temperatures it can 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 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.

- Flexible tubing, for example, silicone of an outer diameter of 10 mm and an inner diameter of 6 mm for making a leakproof connection from the samplers to the sampling pumps without compressing as a result of the pressure difference between ambient atmosphere and the in-line vacuum at the used flow rate.
- Belts or harnesses, which the sampling pumps can conveniently fix for personal sampling.
- Tweezers manufactured from or tipped with PTFE, for handling filters.
- Filter transport cassettes, or similar, if required (see 9.5.1), in which to transport samples to the laboratory.
- Thermometer, of range 0 °C to 50 °C, graduated in divisions of 1 °C or less, for measurement of atmospheric temperature. For applications at temperatures below freezing, the range of the thermometer shall extend to the appropriate desired range.
- Barometer, suitable for measurement of atmospheric pressure.

7.2 Laboratory apparatus

CAUTION — 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).

Alternatively, the glassware may be cleaned with a suitable phosphate-free laboratory detergent using a laboratory washing machine and afterwards rinsed thoroughly with water (6.1).

7.2.3 One-mark volumetric flasks, of capacities up to 2 l, complying with the requirements of ISO 1042.

7.2.4 Plastic labware.

— Screw-cap polyethylene vessels appropriate for the extraction of collected sample filters.

— Beakers of appropriate capacity.

— Disposable filters of PTFE, of pore size 0,45 µm and for use in ion chromatography.

— Disposable syringes of appropriate capacity and with appropriate needles.

— Autosampler vials of appropriate capacity.

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

7.2.6 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.

7.2.7 Ion chromatograph, having the following components:

— pump, capable of delivering a constant flow within the range 0,1 ml/min to 5 ml/min at a pressure of 15 MPa to 150 MPa;

— eluent generation system for the production of a suitable eluent for use with the selected separator column, as an alternative to use of a manually prepared eluent (e.g. see Reference [18]);

— sample injection system, comprising a low dead-volume, non-metallic valve fitted with a sample loop, for injecting the sample solution into the eluent stream;

— guard and separator column, packed with high capacity pellicular anion exchange resin, suitable for resolving chloride, nitrate and bromide from other inorganic anions;

— suppressor module (chemically or electronically suppressed) for ion chromatography, suitable for use with the separator column;

— conductivity detector, flow through, low volume, with a non-metallic flow path.

Components and tubing that come into contact with the sample solution or eluent shall, as far as possible, be comprising inert materials, e.g. polyetheretherketone (PEEK).

8 Occupational exposure assessment

Refer to ISO 20581, EN 689[4] and ASTM E1370[5] for guidance on how to develop an appropriate assessment strategy and for general guidance on measurement strategy.

9 Sampling

9.1 Preliminary considerations

9.1.1 Selection and use of samplers

Select samplers (7.1.1) in accordance with the requirements of the applicable limit value. Size selective samplers shall be designed to collect the appropriate fraction of airborne particles as defined in ISO 7708 and tested in accordance with EN 13205.

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.

If the samplers selected have an internal filter cassette or cartridge that has to be rinsed during sample preparation, this cassette shall be manufactured from a material that does not react with acids.

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

9.1.2 Sampling period

Select a sampling period that is appropriate for the measurement task (see Clause 8) but ensure that it is long enough to enable HCl, HBr or HNO_3 in the air to be determined with acceptable uncertainty at levels of industrial hygiene significance. When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the filter with particulate matter. For example, estimate the minimum sampling time, $t_{\min}$, expressed in minutes, 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 Formula (1):

$$t_{\min} = \frac{m_{\mathrm{LOQ}}}{(q_V \times k \times \rho_{\mathrm{LV}})} \qquad (1)$$

where

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

m_{LOQ} is the limit of quantification, given as mass of the analyte on the sampling substrate, expressed in micrograms;

q_{V} is the design flow rate, expressed in litres per minute, of the sampler;

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

ρ_{LV} is the limit value, expressed in milligrams per cubic metres.

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

When high concentrations of 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).

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 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, for example, if the error is 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 the constant pressure drop, variable area and flow meter.

Consider whether it is necessary to recalculate the concentration of HCl, HBr and HNO_3 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 Formula (A.2) to apply the necessary correction.

The concentration of HCl, HBr and HNO_3 in air is generally stated for actual environmental conditions (temperature, pressure) at the workplace. If the concentration is to be compared with occupational exposure limit values that are referenced at normal temperature and pressure, the concentration should be stated at normal temperature and pressure.

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.

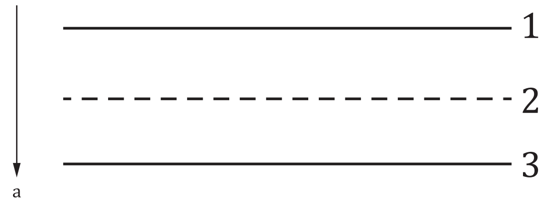
9.2 Preparation for sampling

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 (7.1.1), 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

a 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 (7.1.1) to a sampling pump (7.1.4) using flexible tubing, ensuring that no leaks can occur. Remove the protective cover or plug from each sampler, switch on the sampling pump, attach the flowmeter to the sampler so that it measures the flow through the sampler inlet orifice(s) and set the required volumetric flow rate. Switch off the sampling pump and seal the sampler with its protective cover or plug to prevent contamination during transport to the sampling position.

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

9.2.4 Field blanks

Retain as field blanks one unused loaded sampler (7.1.1) 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

Position the sampler (7.1.1) in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, for example, fastened to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, for example, to a belt around the waist or place it in a convenient pocket.

Give consideration to whether the nature of the 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

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

If static sampling is carried out to characterize the background level of 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 (7.1.1) and switch on the sampling pump. Record the time and volumetric flow rate at the start of the sampling period. If the sampling pump is fitted with an integral timer, check that this is reset to zero. Measure the atmospheric temperature and pressure at the start of the sampling period (see 9.1.3) using the thermometer and barometer (7.1.6), and record the measured values.

NOTE If the temperature or pressure at the sampling position is different from that where the volumetric flow rate was set (see 9.2.3), the volumetric flow rate can change and it can require re-adjustment 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 and record the measured value. Measure the atmospheric temperature and pressure at the end of the sampling period using the thermometer and barometer (7.1.6) 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 calculate the mean atmospheric temperature and pressure (see 9.1.3). 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.

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

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

9.5 Transportation

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

For samplers (7.1.1) that collect airborne particles and/or gases on the filter (see 7.1.1 NOTE 2), remove the filter from each sampler, place in a labelled filter transport cassette and close with a lid. Alternatively, transport samples to the laboratory in the samplers in which they were collected. HCl, HBr or HNO_3 acid are strong acids. Take particular care to prevent the collected sample from coming into contact with the walls of the transport container.

9.5.2 Samplers with an internal filter cassette

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

9.5.3 Samplers of the disposable-cassette type

For samplers (7.1.1) of the disposable-cassette type, transport the samples to the laboratory in the samplers in which they were collected.

9.5.4 Transport of samples to the laboratory

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

Ensure that the documentation which accompanies the samples is suitable for a “chain of custody” to be established (e.g. see ASTM D4840[6]).

9.5.5 Equilibration period

After sampling, store the filters in a clean place for at least four days for equilibration before opening for analysis[11].

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, and filter samples

10.1.1 General

The eluent of the used separation column can be used as an extraction solution and to prepare test solutions for determination of HCl, HBr or HNO_3.

10.1.2 Preparation of filter solutions

Open the filter cassettes or samplers (see 9.5) and transfer each sampling filter into an individual, labelled, screw-cap vessel or beaker, using clean tweezers. 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.

Accurately pipette a suitable volume, for example, 10,0 ml, of extraction solution (see 10.1) into each beaker or screw-cap vessel. Swirl gently to mix the contents, ensuring that the filter remains completely immersed. Treatment for 15 min in an ultrasonic bath is recommended. Allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally.

For preparation of test solutions for analysis by ion chromatography, filter each sample solution through a PTFE filter, for example by using a disposable syringe, dispensing each filtrate into an individual, labelled screw-cap vessel and an autosampler vial.

10.1.3 Preparation of calibration solutions

A multi-point (i.e. the number of points to be consistent with the quality system of the laboratory) calibration shall be constructed within the linear range of the analytical method to cover a proper concentration range of chloride, bromide and nitrate. Accurately pipette appropriate volumes of chloride, bromide and nitrate working standard solution (6.7) into individual, labelled one-mark volumetric flasks, dilute to the mark with water (6.1) or extraction solution (6.5), stopper, and mix thoroughly. Prepare these calibration solutions fresh daily.

10.2 Instrumental analysis

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.

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 $r^2 > 0,999$.

NOTE 1 If $r^2 < 0,999$, it is possible that the removal of an erroneous calibration point and reprocessing of the data will yield an acceptable calibration.

Inject the test solutions (see 10.1) into the ion chromatography system and make measurements for each solution. Use the stored calibration function to determine the chloride, bromide and nitrate concentrations in mg/l.

Analyse the calibration blank solution and a mid-range calibration solution after the initial calibration and then after every 10 test solutions. If the measured concentration of chloride, bromide or nitrate in the continuing calibration blank is above the method limit of detection (LOD), 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.

Analyse reagent blank solutions and laboratory blank solutions and quality control solutions as specified in 10.4 and use the results to monitor the performance of the method as specified.

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 10.1.2) when making dilutions, so that the diluted test solutions and the calibration solutions are matrix-matched, and record the dilution factor.

NOTE 2 For samples expected to have very high concentrations of chloride, bromide or nitrate, it can require dilution of the test solutions before they are first analysed.

10.3 Estimation of limits of detection and quantification

10.3.1 Estimation of the instrumental limit of detection

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

NOTE The instrumental LOD is of use in identifying changes in instrument performance, but it is not a method LOD (see Reference [12]). The instrumental LOD is likely to be lower than the method LOD because it only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample.

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

10.3.2 Estimation of the method limit of detection and limit of quantification

Estimate the method LOD and LOQ under the working analytical conditions using the procedure described in 10.3.1 (which is based on the approach described in Reference [13]) and repeat this exercise whenever the experimental conditions are changed significantly.

Fortify at least 10 sampling filters (7.1.2.2) with chloride, nitrate and bromide near the anticipated method LODs, for example, 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 (6.5.1) by an appropriate factor. Prepare test solutions following the sample dissolution procedure used to prepare the sample test solutions (see 10.2.2).

NOTE An alternative procedure for estimating the method LOD involves the analysis of filter samples fortified with the analyte of interest at values spanning the predicted LOD (see Reference [12]).

10.4 Quality control

10.4.1 Reagent blanks and laboratory blanks

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

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

10.4.2 Quality control solutions

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.

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[7] for general guidance on the use of quality control charts.

10.4.3 Certified reference materials

Suitable CRMs for HCl, HBr or HNO_3 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 Proficiency testing

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 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 according to ISO/IEC Guide 98-3.[3] 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 [14] and [15] 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) by $\sqrt{3}$.

NOTE 3 Systematic errors include 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, ρ_{acid}, expressed in milligrams per cubic metre, using Formula (2):

$$\rho_{\text{acid}} = \frac{(\rho_{\text{anion1}} V_1 f_{\text{d}}) - (\rho_{\text{anion0}} V_0)}{V} f_{\text{c}} \tag{2}$$

where

ρ_{anion0}	is the mean concentration of chloride, bromide and nitrate in the field blank test solutions, expressed in milligrams per litre;
ρ_{anion1}	is the concentration of chloride, bromide and nitrate in the sample test solution, expressed in milligrams per litre;
V	is the volume, expressed in litres, of the air sample;
V_0	is the volume, expressed in millilitres, of the field blank test solutions;
V_1	is the volume, expressed in millilitres, of the sample test solution;
f_d	is the dilution factor (f_d = 1 in the absence of dilution);
f_c	is the factor to convert the anion concentration to an acid concentration (f_c = 1,028 4 for chloride, f_c = 1,012 6 for bromide and f_c = 1,016 3 for nitrate).

12 Method performance

12.1 Sampling efficiency and sample storage

Laboratory testing[16] 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 of sample storage. See Reference [7] for further information.

NOTE The sampling efficiency of the method is diminished if the pre-filter retains some of the sampled acid. Laboratory testing[16] has shown that small amounts of HNO_3 can be retained on certain types of pre-filter and this affects the LOQ of the method if not corrected.

12.2 Limits of quantification

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

The LOQs of the method have been determined[11] to be 1 mg/l 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, for example, 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 to be in the range 96 % to 100 % for hydrochloric and nitric acids, see Reference [11].

12.4.2 Analytical precision

The component of the coefficient of variation of the method that arises from analytical variability, $C_{V,\text{analysis}}$, determined from the analysis of test gas samples, has been found to be in the range 0,4 % to 1,7 % for hydrochloric acid and 1,1 % to 1,9 % for nitric acid, see Reference [11].

12.5 Uncertainty of sampling and analysis method

The expanded uncertainty of the method, using a coverage factor of 2, has been estimated to be <12 % for HCl and HBr and <14 % for HNO_3, see Reference [11]

12.6 Interferences

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.

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 of approximately 20 °C, humidity of approximately 50 %). To estimate the 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 can lead to significant sample loss. Iron oxide was found not to interfere with the determination.

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 document, i.e. ISO 21438-2:2024;

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, expressed 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, expressed 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/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 can 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 LODs, method LODs and LOQs under the working analytical conditions, the measurement uncertainty determined in accordance with ISO/IEC Guide 98-3[3] and, if requested by the customer, quality control data;

q) any operation not specified in this document or regarded as optional;

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

s) the data 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.