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Workplace atmospheres — Determination of inorganic acids by ion chromatography —

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

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

Partie 1: Acides non volatils (acide sulfurique et acide phosphorique)

Reference number
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Foreword

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

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 21438-1 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)*

The following parts are under preparation:

— *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 particulate acids like sulfuric acid or phosphoric acid compounds. 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 particulate acids in use in industry. It will be of benefit to: agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; and industrial users of sulfuric and phosphoric acids, and their workers.

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

Workplace atmospheres — Determination of inorganic acids by ion chromatography —

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

1 Scope

This part of ISO 21438 specifies a method for the determination of the time-weighted average mass concentration of sulfuric acid and phosphoric acid in workplace air by ion chromatography.

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 0,005 mg to 2,0 mg of sulfuric acid and phosphoric acid per sample, without dilution.

The concentration range of sulfuric acid and phosphoric acid in air for which the measuring procedure is applicable is determined by the sampling method selected by the user. For an air sample of volume 1 m^3, the working range is approximately 0,005 mg m^{-3} to 2,0 mg m^{-3}.

The method is not applicable to the determination of sulfur trioxide.

The procedure does not allow differentiation between the acids and their corresponding salts if both are present in the air.

The procedure does not allow differentiation between phosphoric acid and diphosphorus pentoxide (phosphoric anhydride) if both are present in the workplace.

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*

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

[EN 1540:1998[1], definition 3.9]

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 is a plane through this line, the top of the head and the larynx

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

NOTE 2 Adapted from EN 1540:1998[1], definition 3.8.

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], definition 3.36]

3.1.7
time-weighted average concentration
TWA concentration
concentration of a chemical agent in the atmosphere, averaged over the 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 (see Reference [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 (see Reference [3]).

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

[EN 1540:1998[1], definition 3.20]

3.2 Particle size fraction definitions

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

[ISO 7708:1995, definition 2.4]

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

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

[ISO 7708:1995, definition 2.3]

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 particle concentration.

[ISO 7708:1995, definition 2.13]

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], definition 3.20]

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

[EN 1540:1998[1], definition 3.21]

3.3.3
sampling instrument
sampler
a device for collecting airborne particles

NOTE This definition is formulated for the purposes of this part of ISO 21438.

EXAMPLES Instruments used to collect airborne particles include sampling heads, filter holders, filter cassettes, etc.

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 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 sulfate and phosphate in the calibration blank solution is taken to be zero.

3.4.3
calibration solution
solution prepared by dilution of the working standard solution, containing sulfate and phosphate at concentrations that are suitable for use in calibration of the analytical instrument

3.4.4
extraction solution
solvent or solution used to solubilise 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 used for sampling, that does not leave the laboratory

3.4.7
linear dynamic range
range of concentrations over which the calibration curve for sulfate or phosphate is linear

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

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

3.4.9
sample dissolution
process of obtaining a solution containing sulfate and phosphate 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 sulfate and/or phosphate 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 sulfate and phosphate at concentrations that are better suited to preparation of calibration solutions than the concentration of sulfate and phosphate 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 A coverage factor, k, is typically in the range 2 to 3.

[ISO Guide 98:1995[4], definition 2.3.6]

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 Guide 98:1995[4], definition 2.3.4]

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

[ISO Guide 98:1995[4], definition 2.3.5]

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 characterises 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 characterises 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 characterised by standard deviations. The other components, which can also be characterised by standard deviations, are evaluated from assumed probability distributions based on experience or other information. ISO Guide 98:1995[4] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

NOTE 3 Adapted from ISO Guide 99:1996[5], definition 3.9.

4 Principle

4.1 A known volume of air is drawn through a filter to collect acid mist. The filter is mounted in a sampler designed to collect the inhalable fraction of airborne particles (see 7.1.1).

4.2 The collected sample is then treated with water (6.1) or eluent (see 10.1.1), without heating, to extract sulfuric and phosphoric acids.

4.3 Aliquots of the sample solution are subjected to ion chromatography in order to separate the extracted sulfate and/or phosphate from other anions. Following this separation, the anions are measured using a conductivity detector.

4.4 Analytical results are obtained by plotting the measured conductivity as a function of concentration. They can be used for assessment of occupational exposure to sulfuric acid and phosphoric acid (and diphosphorus pentoxide) in air.

5 Requirement

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

6 Reagents

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

NOTE Sulfates and phosphates are found ubiquitously in the environment and the presence of sulfates and phosphates in reagents can lead to high blank values.

6.1 Water, from a purification system that delivers ultrapure water having a resistivity greater than 0,18 MΩ·m (18 MΩ·cm).

6.2 Reagents for chemically suppressed ion chromatography.

NOTE The sodium carbonate/sodium hydrogencarbonate eluent prescribed below is an example that can be used with separator columns for analysis of phosphate and sulfate using 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.

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

6.2.2 Sodium hydrogencarbonate ($NaHCO_3$), mass fraction >99,5 %.

6.2.3 Sodium carbonate/sodium hydrogencarbonate extraction and eluent stock solution, containing 0,27 mol l^{-1} Na_2CO_3 and 0,03 mol l^{-1} $NaHCO_3$.

Dissolve 2,86 g of sodium carbonate (6.2.1) and 0,25 g sodium hydrogencarbonate (6.2.2) 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 (6.1), stopper and mix thoroughly.

6.2.4 Sodium carbonate/sodium hydrogencarbonate extraction and eluent solution, 0,002 7 mol l^{-1} Na_2CO_3 and 0,000 3 mol l^{-1} $NaHCO_3$.

Transfer 10 ml of sodium carbonate/sodium hydrogencarbonate stock solution (6.2.3) to a 1 l one-mark volumetric flask (7.2.2.1), dilute to the mark with water (6.1), stopper and mix thoroughly.

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

6.3 Reagents for electronically suppressed ion chromatography.

NOTE The phthalic acid and borate/gluconate solutions prescribed below are two examples of eluents used for analysis of phosphate and sulfate 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.

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

6.3.2 Acetonitrile (C_2H_3N), HPLC grade.

6.3.3 Methanol (CH_4O), HPLC grade.

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

6.3.5 Boric acid (H_3BO_4), mass fraction >99,8 %.

6.3.6 D-Gluconic acid ($C_6H_{12}O_7$) **solution**, mass fraction approximately 50 % of D-gluconic acid in water (6.1).

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

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

Dissolve 1,66 g of phthalic acid (6.3.1) in a 9+1 volume ratio mixture of acetonitrile (6.3.2) and methanol (6.3.3), in a suitable 1 l vessel and mix thoroughly.

6.3.9 Lithium hydroxide solution, 1 mol l^{-1}.

Dissolve 4,2 g of lithium hydroxide monohydrate (6.3.4) 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 (6.1), stopper and mix thoroughly.

6.3.10 Phthalic acid extraction and eluent solution, e.g. 0,005 mol l^{-1} phthalic acid, pH 4,9.

Transfer an appropriate volume, e.g. 50 ml, of phthalic acid solution (6.3.8) to a 1 l one-mark volumetric flask, add approximately 900 ml of water (6.1), adjust to pH 4,9 with lithium hydroxide solution (6.3.9) and dilute to the mark with water (6.1).

6.3.11 Borate/gluconate extraction and eluent stock solution.

Dissolve 17 g of boric acid (6.3.5), 4,8 g of lithium hydroxide monohydrate (6.3.4), 8,8 ml of D-gluconic acid (6.3.6) and 62,5 ml of glycerol (6.3.7) 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 (6.1), stopper and mix thoroughly.

6.3.12 Borate/gluconate extraction and eluent solution.

Transfer 15 ml of borate/gluconate stock solution (6.3.11) and 120 ml of acetonitrile (6.3.2) to a 1 l one-mark volumetric flask and dilute to the mark with water (6.1), stopper and mix thoroughly.

6.4 Sulfate and phosphate standard solutions.

6.4.1 Sulfate stock standard solution.

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

6.4.2 Phosphate stock standard solution.

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

6.4.3 Sulfate and phosphate working standard solution, 200 mg l^{-1} of sulfate and phosphate.

Accurately pipette an appropriate volume, e.g. 4 ml, of the sulfate stock standard solution (6.4.1) and an appropriate volume, e.g. 4 ml, of the phosphate stock standard solution (6.4.2) 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.

The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.

NOTE 1 In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static sampling.

NOTE 2 Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge that can be removed from the sampler to enable this material to be easily recovered.)

NOTE 3 Reference [7] gives examples of inhalable samplers with the potential to meet the requirements of EN 13205 that were or had been available on the market up to 2004, including published reports on their performance.

7.1.2 Filters, of a diameter suitable for use with the samplers (7.1.1), with a collection efficiency $\geqslant$ 99,5 % for particles with a 0,3 µm diffusion diameter (see ISO 7708:1995, 2.2), and manufactured from a material that is compatible with the sample preparation and analysis method.

Sulfuric acid and phosphoric acid are strong acids. They react, e.g. by dehydration, with many organic and polymeric materials, and destroy the filter material. Therefore, correct selection of the filter used for sample collection is of paramount importance. In particular, the filter has to be manufactured from a material that does not react with the acids. Also, some filters, e.g. glass fibre filters, can contain metals, e.g. barium, that react with sulfuric and/or phosphoric acids to produce insoluble salts. The following filter types are generally suitable for use:

— polyvinyl chloride (PVC) membrane filters, of pore size 5 µm or less;

— polytetrafluoroethylene (PTFE) membrane filters, of pore size 5 µm or less; and

— quartz fibre filters.

Sulfates and phosphates are found ubiquitously in the environment and the presence of sulfates and phosphates in filter materials can lead to high blank values. It is therefore essential to check the blank values of each batch of filters used.

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

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

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

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

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

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

An integral timer is a highly desirable additional feature.

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

EN 1232[2] and EN 12919[9] 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; and

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[9] appropriate action should be taken to ensure that the performance requirements are met. For instance, at sub-zero temperatures it might be necessary to keep the pump warm.

7.1.4 Flowmeter, portable, with an accuracy that is sufficient to enable the volumetric flow rate (see 9.1.1.2) to be measured to within ±5 %.

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

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

7.1.5 Ancillary equipment.

7.1.5.1 Flexible tubing, of a diameter suitable for making a leakproof connection from the samplers (7.1.1) to the sampling pumps (7.1.3).

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

7.1.5.3 Tweezers, manufactured from or tipped with PTFE, for loading and unloading filters into samplers (9.2.2, 9.5.3.2 and 10.1.2.2.1).

7.1.5.4 Filter transport cassettes, or similar, if required (see 9.5.1), in which to transport samples to the laboratory.

7.1.5.5 Thermometer, of range 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.

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

7.2 Laboratory apparatus

Usual laboratory apparatus, and in particular the following. Disposable plastic labware is generally preferable to glassware.

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

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 laboratory detergent using a laboratory washing machine and afterwards rinsed thoroughly with water (6.1).

7.2.2.1 One-mark volumetric flasks, of capacities between 10 ml and 1 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 capacities between 10 ml and 1 l.

7.2.3.2 Screw-cap polyethylene vessels, of capacity 10 ml.

7.2.3.3 Beakers, of capacity 50 ml.

7.2.3.4 Graduated centrifuge tubes, with caps, of capacity 15 ml.

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

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

7.2.3.7 Disposable syringes, of capacity 2 ml or 5 ml, with 60 mm × 0,6 mm needles.

7.2.3.8 Autosampler vials, of capacity 1,5 ml to 2 ml.

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

7.2.5 Ultrasonic bath, preferably with a timer, suitable for use in the ultrasonic extraction method for sulfuric acid or phosphoric acid (see 10.1.2.1.1).

7.2.6 Ion chromatograph, having the components listed in 7.2.6.1 to 7.2.6.10, inclusive. 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 min^{-1} to 5 ml min^{-1} at a pressure of 15 MPa to 150 MPa.

7.2.6.2 **Eluent generation system**, for producing an eluent suitable for use with the selected separator column (see 7.2.6.5), as an alternative to use of a manually prepared eluent (see e.g. Reference [10]).

7.2.6.3 **Sample injection system**, comprising 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 (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 sulfates and phosphates from other inorganic anions.

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

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

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

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

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

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

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

7.2.6.10 Eluent reservoir, comprising of a container suitable for storing eluent or water (6.1) 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 (area) samples. Refer to relevant international, European or national standards {e.g. EN 482[6], EN 689[11], ASTM E 1370[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 sulfuric acid and phosphoric acid shall normally be determined by personal sampling, since the concentration of sulfuric acid and phosphoric acid 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 the Note to 9.1.2.1 for an example of such a situation); to characterise

the background level of sulfuric acid and phosphoric acid 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 may be performed to provide information on the likely pattern of concentration of chemical agents. They can be used to identify locations and periods of elevated exposure and to set the duration and frequency of sampling for measurements for comparison with limit values. Emission sources can be located and the effectiveness of ventilation or other technical measures can be estimated (see EN 482[6]).

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 may be performed to obtain relatively crude information on the exposure level in order to decide whether an exposure problem exists at all, and if so to appraise its possible seriousness. They may also be used to determine if the exposure is well below or well above the limit value (see EN 482[6]).

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” (see EN 689:1995[11], 5.2.3.2).

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 (see EN 482[6]).

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).

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

8.4.5.2 Periodic measurements

Periodic measurements are performed to determine whether exposure conditions have changed since measurements for comparison with limit values were made, or whether control measures remain effective (see EN 482[6]).

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 appropriate fraction of airborne particles, as defined in ISO 7708, according to which particle size fraction the exposure limit(s) for the acid(s) of interest is applicable.

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

If the samplers selected have an internal filter cassette or cartridge that has to be rinsed during sample preparation (see 9.5.2.2 and 10.1.2.2.3), this cassette shall be manufactured from a material that does not react with acids.

9.1.1.2 Use the samplers at their design flow rate and in accordance with the instructions provided by the manufacturer. See CEN/TR 15230[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 sulfuric acid or phosphoric acid in to be determined with acceptable uncertainty (see 3.5.8) at levels of industrial hygiene significance. For example, estimate the minimum sampling time, t_{min}, in minutes, required to ensure that the amount collected is above the lower limit of the working range of the analytical method when sulfuric acid or phosphoric acid is present in the test atmosphere at a concentration of 0,1 times its limit value, using Equation (1):

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

where

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

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

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

NOTE If the minimum sampling time is not short enough for the method to be useful for the intended measurement task, consider the possibility of using a sampler designed to be used at a higher flow rate (see 9.3.2.1).

9.1.2.2 When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the 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 whether the indicated volumetric flow rate of the flowmeter (7.1.4) is dependent upon temperature and pressure. Consider whether the difference between the atmospheric temperature and pressure at the time of calibration of the flowmeter and during sampling is likely to be great enough to justify making a correction to take this into account, e.g. if the error could be greater than ±5 %. If a correction is necessary, measure and record the atmospheric temperature and pressure at which the calibration of the flowmeter was checked (see 7.1.4), 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 flowmeter.

9.1.3.2 Expression of results

Consider whether it is necessary to recalculate the concentration of sulfuric acid or phosphoric acid in air to reference conditions (see ISO 8756[13]). 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 sulfuric acid or phosphoric acid in air is generally stated for actual environmental conditions (temperature, pressure) at the workplace.

9.1.4 Sample handling

To minimise the risk of damage or contamination, only handle filters (7.1.2) in a clean area where the concentration of sulfuric acid and phosphoric acid in air is minimal and using PTFE tweezers (7.1.5.3).

9.1.5 Sampling interferences

9.1.5.1 Sulfuric acid is widely used in industry (e.g. in the extraction of rock phosphates and other ores, in metal processing, in electroplating, for sulfonation, as a component of nitrating acids, as a desiccant, and in lead batteries). At many workplaces, not only sulfuric acid is present; sulfates or other sulfur compounds (e.g. sulfur dioxide, or sulfur trioxide and dithiocarbonic acid derivatives) can occur. Similarly, phosphoric acid is widely used in industry (e.g. in the production of phosphate fertilisers, phosphates, porcelain cements, as a polymerisation catalyst, in metal processing, as an etching agent and in the production of flame retardants). At many workplaces, not only phosphoric acid is present; phosphates, diphosphorus pentoxide or other phosphorus compounds (e.g. metaphosphates) may also be evident. Consider how to address the problem of possible interferences before commencing with sampling (see 9.1.5.2 and 9.1.5.3).

9.1.5.2 If results are required for comparison with a limit value for sulfuric acid and/or phosphoric acid, and it is expected that sulfates or phosphates are present in the test atmosphere, correct results to the free acid content by collecting and analysing a sample from the emission source, e.g. pickling bath solution (see 12.6.2).

9.1.5.3 If results are required for comparison with separate limit values for phosphoric acid and diphosphorus pentoxide, it is not possible to distinguish between the two chemical agents. Therefore, if both substances could be present in the test atmosphere (12.6.3), report results as phosphoric acid and add a note to the test report to the effect that the reported phosphoric acid concentration includes any diphosphorus pentoxide.

9.1.5.4 When present in workplace air, sulfur trioxide, sulfur dioxide and volatile organic sulfur compounds exist as gases or vapours and do not interfere with the sampling method.

9.2 Preparation for sampling

9.2.1 Cleaning of samplers

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

9.2.2 Loading the samplers with filters

Load clean samplers (see 9.2.1) with suitable membrane or quartz fibre filters (7.1.2), label each sampler so that it can be uniquely identified and seal with its protective cover or plug to prevent contamination.

9.2.3 Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of sulfuric acid and phosphoric acid is minimal.

Connect each loaded sampler (see 9.2.2) to a sampling pump (7.1.3) using flexible tubing (7.1.5.1), ensuring that no leaks can occur. Remove the protective cover or plug from each sampler, switch on the sampling pump, attach the flowmeter (7.1.4) 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 stabilise before setting the volumetric flow rate.

9.2.4 Field blanks

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

9.3 Sampling position

9.3.1 Personal sampling

9.3.1.1 Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, e.g. fastened to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, e.g. to a belt (7.1.5.2) around the waist, or place it in a convenient pocket.

9.3.1.2 Give consideration to whether the nature of the process is likely to result in a significant difference between the actual exposure of the worker and the concentration of sulfuric acid or phosphoric acid 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 characterise the background level of sulfuric acid or phosphoric acid in the workplace, select a sampling position that is sufficiently remote from the work processes, such that results will not be directly affected by sulfuric acid or phosphoric acid 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 (7.1.5.5) and barometer (7.1.5.6), and record the measured values.

NOTE If the temperature or pressure at the sampling position is different from that where the volumetric flow rate was set (see 9.2.3), the volumetric flow rate could change and it might need to be readjusted before sampling.

9.4.2 At the end of the sampling period (see 9.1.2), record the time and calculate the duration of the sampling period. Check the malfunction indicator 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 flowmeter (7.1.4), 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 (7.1.5.5) and barometer (7.1.5.6), 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, if appropriate (see 9.1.3), calculate the mean atmospheric temperature and pressure. Calculate the volume, in litres, of air sampled at atmospheric temperature and pressure by multiplying the mean flow rate, in litres per minute, by the duration, in minutes, of the sampling period.

9.5 Transportation

9.5.1 Samplers that collect airborne particles on the filter

9.5.1.1 For samplers that collect airborne particles on the filter (see Note 2 to 7.1.1), except when using quartz fibre filters (see 9.5.1.2), remove the filter from each sampler, place in a labelled filter transport cassette (7.1.5.4) and close with a lid. Alternatively, transport samples to the laboratory in the samplers in which they were collected. Sulfuric acid and phosphoric acid are strong acids. Take particular care to prevent the collected sample from coming into contact with the walls of the transport container.

9.5.1.2 When using quartz fibre filters, place the filter in a screw-cap polyethylene vessel (7.2.3.2) immediately after sampling using clean PTFE tweezers (7.1.5.3), accurately pipette 4,0 ml of extraction solution (see 10.1.1) into the vessel, close with a plastic cap and shake gently.

NOTE Anecdotal evidence (Reference [24]) suggests that it is necessary to extract sulfate from quartz fibre filters immediately after sampling to achieve quantitative recovery of sulfuric acid.

9.5.2 Samplers with an internal filter cassette

9.5.2.1 For samplers with an internal filter cassette (see Note 2 to 7.1.1), except when using quartz fibre filters (see 9.5.2.2), remove the filter cassette from each sampler and fasten with its lid or transport clip.

9.5.2.2 When using quartz fibre filters, place the filter in a screw-cap polyethylene vessel (7.2.3.2) immediately after sampling using clean PTFE tweezers (7.1.5.3), rinse the internal surfaces of the filter cassette into the sample vessel with 4,0 ml of extraction solution (see 10.1.1), close with a plastic cap and shake gently.

9.5.3 Samplers of the disposable cassette type

9.5.3.1 For samplers of the disposable cassette type, except when using quartz fibre filters (see 9.5.3.2), transport the samples to the laboratory in the samplers in which they were collected.

9.5.3.2 When using quartz fibre filters, place the filter in a screw-cap polyethylene vessel (7.2.3.2) immediately after sampling using clean PTFE tweezers (7.1.5.3), rinse the internal surfaces of the filter cassette into the sample vessel with 4,0 ml of extraction solution (see 10.1.1), close with a plastic cap and shake gently.

NOTE Anecdotal evidence suggests that it is necessary to extract sulfate from quartz fibre filters immediately after sampling to achieve quantitative recovery of sulfuric acid.

It is possible to carry out the extraction in the samplers if they are of sufficient capacity and are watertight when the sample inlet and outlet orifices are sealed with their protective plugs. In this case, the extraction solution should be added to the sampler via the air inlet orifice, the sample inlet and outlet orifices should be sealed with their protective plugs and the sampler should be maintained in an upright position during transportation.

9.5.4 Transport of samples to the laboratory

9.5.4.1 Transport the samples (9.5.1 to 9.5.3) to the laboratory in a container which has been designed to prevent damage to the samples in transit, and which has been labelled to ensure proper handling.

9.5.4.2 Ensure that the documentation which accompanies the samples is suitable for a "chain of custody" to be established (see, for example, ASTM D 4840[14]).

10 Analysis

CAUTION — Use suitable personal protective equipment (including 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 the eluent (6.2.4, 6.3.10 or 6.3.12, depending on the analytical technique and separator column used) to prepare test solutions for determination of sulfuric acid or phosphoric acid.

10.1.2 Preparation of test solutions from filter sampling

10.1.2.1 Quartz fibre filters

10.1.2.1.1 Swirl each screw-cap polyethylene vessel or sampling cassette (9.5.3.2) to mix the contents, ensuring that the filter remains completely immersed. Agitate for 15 min in an ultrasonic bath (7.2.5) and then allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally.

If the extraction is to be carried out in a sampler of the disposable cassette type (see 9.5.3.2), the protective plug should be removed from the sample inlet orifice and the sampler should be maintained in an upright position whilst in the ultrasonic bath to avoid spillage and contamination of the sample solution.

10.1.2.1.2 Filter each sample solution through a membrane filter (7.2.3.6) using a disposable syringe (7.2.3.7), dispensing each filtrate into an individual, labelled, autosampler vial (7.2.3.8).

10.1.2.2 PVC and PTFE filters

10.1.2.2.1 Open the filter transport cassettes, sampler filter cassettes or samplers (see 9.5) and transfer each filter into an individual, labelled 50 ml beaker (7.2.3.3) using clean PTFE tweezers (7.1.5.3), ensuring that the side of the filter on which the sample was collected is facing upwards. Follow the same procedure for the blank filters (see 9.2.4).

It is possible to carry out the extraction in samplers of the disposable cassette type if they are of sufficient capacity and are watertight when the sample outlet orifice is sealed with its protective plug. In this case, the extraction solution (see 10.1.2.2.2) should be added to the sampler via the air inlet orifice and the samplers should be maintained in an upright position whilst in the ultrasonic bath (see 10.1.2.2.3) to avoid spillage and contamination of the sample solutions.

10.1.2.2.2 Accurately pipette 4,0 ml of extraction solution (see 10.1.1) into each beaker. If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the sampler form part of the sample (see Note 2 to 7.1.1), use the extraction solution to wash carefully any particulate material adhering to the internal surfaces of the sampler into the beaker. In the case of PTFE filters, add 0,1 ml of ethanol because of their hydrophobic nature.

10.1.2.2.3 Swirl gently to mix the contents, ensuring that the filter remains completely immersed. Agitate for 15 min in an ultrasonic bath (7.2.5) and then allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally.

10.1.2.2.4 Filter each sample solution (10.1.2.2.3) through a membrane filter (7.2.3.6), e.g. by using a disposable syringe (7.2.3.7), dispensing each filtrate into an individual, labelled, autosampler vial (7.2.3.8).

10.1.3 Preparation of calibration solutions

Prepare a minimum of five calibration solutions to cover a concentration range from 2 mg l^{-1} to 20 mg l^{-1} of sulfate and phosphate. Accurately pipette appropriate volumes of sulfate and phosphate working standard solution (6.4.3) into individual, labelled one-mark volumetric flasks (7.2.2.1), dilute to the mark with water (6.1), stopper and mix thoroughly. Prepare these calibration solutions fresh daily.

10.2 Instrumental analysis

10.2.1 Setting up the instrument

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

10.2.1.2 Install a sample loop that gives a suitable injection volume, e.g. 50 µl.

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 (6.2.4, 6.2.5, 6.3.10 and 6.3.12) to a value that is compatible with the columns used, e.g. 1,5 ml min^{-1}.

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

10.2.2 Analysis

10.2.2.1 Inject the calibration solutions (10.1.3) into the ion chromatography system in order of increasing concentration and measure the conductivity of the sulfuric acid or phosphoric acid peak for each calibration solution, in peak area mode.

10.2.2.2 Use the instrument's computer to generate a calibration function using a linear regression. Repeat the calibration if the coefficient of determination, $r^2 \leqslant 0{,}999$.

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

10.2.2.3 Inject the laboratory blank solutions (see 10.4.1) and the blank and sample test solutions (see 10.1.2) into the ion chromatography system and make conductivity measurements for each solution. Use the stored calibration function (10.2.2.2) to determine the concentration, in milligrams per litre, of sulfuric acid or phosphoric acid.

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

10.2.2.5 Analyse reagent blank solutions and laboratory blank solutions, as specified in 10.4.1.1, 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 concentrations of sulfate or phosphate are found to be above the upper limit of the linear calibration range, dilute the test solutions in order to bring them within the linear range and repeat the analysis. Add an appropriate volume of extraction solution (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, f_{dilution}.

NOTE For samples expected to have very high concentrations of sulfate or phosphate, it may prove 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 limits

10.3.1.1 Estimate the instrumental detection limits for sulfate and phosphate 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 sulfate and phosphate concentrations near the anticipated instrumental detection limits, by diluting the working standard solution (6.4.3) by an appropriate factor.

10.3.1.3 Make at least 10 ion chromatographic measurements on the test solution (10.3.1.2) and calculate the instrumental detection limits for sulfate and phosphate as three times the sample standard deviation of the mean concentration values.

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 [15]) and repeat this exercise whenever the experimental conditions are changed significantly.

10.3.2.2 Fortify at least 10 filters (7.1.2) with sulfate and phosphate near the anticipated method detection limit, e.g. 1,5 µg of sulfate or phosphate, by spiking each filter with 0,1 ml of a solution prepared by diluting the working standard solution (6.4.3) by an appropriate factor.

10.3.2.3 Make ion chromatographic measurements on the test solutions derived from each spiked filter (10.3.2.2), after carrying out extraction of the filters, and calculate the method detection limit and the quantification limit as three times and 10 times the sample standard deviation of the mean concentration value, respectively.

NOTE An alternative procedure for estimating the instrumental 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 according to 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 recur.

10.4.2 Quality control solutions

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

10.4.2.2 Monitor the performance of the method by plotting control charts of the relative percentage recoveries and of the relative percentage differences between the spiked samples and the spiked duplicate samples. If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action, and reanalyse the samples if necessary. See ASTM E 882[17] for general guidance on the use of quality control charts.

10.4.3 Certified reference materials

If available, suitable certified reference materials (CRMs) for sulfuric acid or phosphoric acid shall be analysed prior to routine use of the method to establish that the percentage recovery relative to the certified value is satisfactory. CRMs are available from the European Commission and National Institute for Standards and Technology (NIST), among other sources.

10.4.4 External quality assessment

If laboratories carry out sulfuric acid or phosphoric acid 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 a database such as the European Information System on Proficiency Testing Schemes (EPTIS, 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 Guide 98:1995[4]. The first step is to construct a cause and effect diagram (see Reference [19]) 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 [19] and [20] 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 √3.

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

11 Expression of results

Calculate the mass concentration, ρ_{acid}, in milligrams per cubic metre, of sulfuric acid or phosphoric acid in the air samples at ambient conditions, using Equation (2):

$$\rho_{acid} = \frac{(\rho_{anion,1} \times V_1 \times f_{dilution}) - (\rho_{anion,0} \times V_0)}{V} \times f_{conversion} \quad (2)$$

where

$\rho_{anion,0}$ is the mean concentration, in milligrams per litre, of sulfate or phosphate in the field blank test solutions;

$\rho_{anion,1}$ is the concentration, in milligrams per litre, of sulfate or phosphate in the sample test solution;

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;

$f_{dilution}$ is the dilution factor (for neat solutions $f_{dilution}$ = 1);

$f_{conversion}$ is the factor to convert from anion to acid concentration ($f_{conversion}$ = 1,021 for sulfate; $f_{conversion}$ = 1,031 8 for phosphate).

12 Method performance

12.1 Sample collection and stability

Laboratory testing with generated atmospheres of sulfuric acid mist yielded a collection efficiency of >95 % over the range 0,5 mg m^{-3} to 10 mg m^{-3} of sulfuric acid on 0,45 µm pore-size PTFE filters (Reference [21]); and >95 % recovery of sulfuric acid or phosphoric acid was found four weeks after sample collection. On quartz fibre filters, 97 % to 100 % recovery of sulfuric acid or phosphoric acid was found four weeks after sample collection (Reference [23]).

12.2 Quantification limits

The quantification limit of the method for both phosphate and sulfate, estimated as prescribed in 10.3.2, is 1 mg l^{-1}. For a sample solution volume of 4 ml and an air sample volume of 420 l, this is equivalent to 0,01 mg m^{-3} of sulfuric acid or phosphoric acid.

12.3 Upper limits of the analytical range

The upper limit of the analytical range is governed by the maximum permissible loading of the sample filter. It has been demonstrated (Reference [23]) that no breakthrough occurs for quartz fibre filters at sample loadings of up to 1 mg.

NOTE Anecdotal evidence suggests that breakthrough of phosphoric and sulfuric acids can occur for certain filter types at high sample loadings.