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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.

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

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

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 21438-1:2007), which has been technically revised throughout.

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 particulate acids such as 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 document 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 the ISO 21438 series 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 document 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 anions are detected by conductivity.

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

The method does not apply to the determination of sulfur trioxide.

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

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

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 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 sulfate and phosphate 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 sulfate and phosphate 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 sulfate and phosphate from a sample, which might or might not involve complete dissolution of the sample

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

Note 1 to entry: A sample solution can sometimes need to be subjected to further operations, e.g. 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 sulfate and/or phosphate 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 sulfate and phosphate at concentrations that are better suited to preparation of *calibration solutions* (3.3) than the concentration of sulfate and phosphate in the stock standard solutions

4 Principle

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 required particle fraction of airborne particles (see 7.1.1).

Currently, limit values in different countries exist for sulfuric acid either as “total particulate mass”, defined by the performance of a sampler, or in the inhalable or the thoracic size selective fraction. A suitable sampling device for the applicable particle fraction shall be used considering the existing limit value/particle fraction.

The collected sample is then treated with eluent and ultrasonic application, without heating, to extract sulfuric and phosphoric acids.

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

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

5 Requirement

The measuring procedure shall conform to any relevant international, European or national standard which specifies performance requirements for procedures for measuring chemical agents in workplace air (e.g. ISO 20581[3]).

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 1 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 of grade 1 (in accordance with ISO 3696).

NOTE 2 State of art water purification systems deliver water of grade 1 with higher quality than specified in ISO 3696:1987 (e.g. resistivity greater than 18 MΩ·cm).

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

6.3 Sodium hydrogencarbonate ($NaHCO_3$), anhydrous, mass fraction > 99,9 %.

NOTE 3 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.

6.4 Sodium carbonate/sodium hydrogen carbonate extraction and eluent stock solution.

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

6.5 Sodium carbonate/sodium hydrogen carbonate 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.

6.6 Sulfate and phosphate 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 stock solution.

6.7 Sulfate and phosphate calibration solutions.

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

6.8 Sulfate and phosphate check-standard.

Use a certified reference material (CRM) as described in 10.4.3 with a certificate of its concentration, e.g. 400 mg/l for sulfate and 600 mg/l for phosphate, traceable to national standards. Observe the manufacturer's expiry date or recommended shelf-life.

6.9 Sulfate and phosphate check-standard working solution.

The check-standard working solution should be in the middle of the calibration range. Pipette a proper volume of the sulfate and phosphate check-standard (6.8) to create a check-standard with the eluent (6.4). Prepare this solution fresh for every calibration. If necessary, create a check-standard working solution for sulfate and phosphate separately.

7 Apparatus

7.1 Sampling equipment

7.1.1 Samplers as required to collect samples consistent with applicable limit values. The performance of samplers shall be in accordance with EN 13205 where specific size-selective fractions are stipulated.

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 PD CEN/TR 15230[9] gives examples of inhalable samplers with the potential to meet the requirements of EN 13205, including published reports on their performance.

NOTE 4 Reference [13] discusses the relationship between inhalable and thoracic fractions of sulfuric acid in workplaces.

7.1.2 Filters, of a diameter suitable for use with the samplers, with a collection efficiency ≥ 99 % for particles with a 0,3 µm diffusion diameter 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:

- binder-free quartz fibre filters;
- polyvinyl chloride (PVC) membrane filters, of pore size 5 µm or less;
- polytetrafluoroethylene (PTFE) membrane filters, of pore size 5 µm or less;

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, in accordance with ISO 13137[2], should be used.

If the sampling pump is used outside the range of conditions specified in ISO 13137[2] 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.

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

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

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

7.1.5 Ancillary equipment:

- **Flexible tubing**, e.g. silicone of an outer diameter of 10 mm and an inner diameter of 6 mm for making a leakproof connection from the samplers to the sampling pumps without compressing as a result of the pressure difference between ambient atmosphere and the in-line vacuum at the used flow rate of 3,5 l min^{-1}.
- **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 — 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, conforming to 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, conforming to the requirements of ISO 1042.

7.2.4 Plastic labware:

- **Screw-cap polyethylene vessels proper for the extraction** of collected sample filters.
- **Beakers**, of appropriate capacity.
- **Disposable membrane filters, of PTFE, of pore size 0,45 µm**, for use in ion chromatography.
- **Disposable syringes**, of appropriate capacity, appropriate needles.
- **Autosampler vials**, of appropriate capacity.

7.2.5 Piston-operated volumetric instruments, of capacities of 50 µl to 10 ml, conforming to the requirements of ISO 8655-1, and tested in accordance with ISO 8655-6; pipettors, conforming to 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 sulfuric acid or phosphoric acid.

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

- **Pump**, capable of delivering a constant flow within the range 0,1 ml/min to 5 ml at a pressure of 15 MPa to 150 MPa.
- **Eluent generation system**, for producing an eluent suitable for use with the selected separator column, as an alternative to use of a manually prepared eluent (see, for example, Reference [23]).
- **Sample injection system**, comprising a low dead-volume, non-metallic valve fitted with a sample loop, for injecting the sample solution into the eluent stream.
- **Guard and separator column,** packed with high capacity pellicular anion exchange resin, suitable for resolving sulfates and phosphates from other inorganic anions.
- **Suppressor module (chemically suppressed or electronically suppressed) for ion chromatography**, suitable for use with the separator column.
- **Conductivity detector**, flow through, low volume, with a non-metallic flow path.

8 Occupational exposure assessment

Refer to relevant international, European or national standards (e.g. ISO 20581[3], EN 689[10], ASTM E1370[8]) 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) according to 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 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 and 10.1.3), 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 PD CEN/TR 15230[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 sulfuric acid or phosphoric acid to be determined with acceptable uncertainty at levels of industrial hygiene significance. When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the filter with particulate matter. For example, estimate the minimum sampling time, t_{min}, in minutes, required to ensure that the amount collected is above the lower limit of the working range of the analytical method when sulfuric acid or phosphoric acid is present in the test atmosphere at a concentration of 0,1 times its limit value, using Formula (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.

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

9.1.3 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, 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.

Consider whether it is necessary to recalculate the concentration of sulfuric acid or phosphoric acid in air to reference conditions (see ISO 8756[1]). 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 formula given in Clause A.2 to apply the necessary correction.

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

9.1.4 Sample handling

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

9.1.5 Sampling interferences

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, 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 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) can also be evident. Consider how to address the problem of possible interferences before commencing with sampling; see the following:

— 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).

— 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 (see 12.6), 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.

NOTE 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 drying before reassembly. Alternatively, use a laboratory washing machine.

NOTE Some samplers are single use and disposable and do not require cleaning before use.

9.2.2 Loading the samplers with filters

Load clean samplers (see 9.2.1) with suitable collecting 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.

NOTE Some samplers are pre-loaded with filters by the manufacturer.

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 to a sampling pump 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 from each batch of ten prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters.

9.3 Sampling position

9.3.1 Personal sampling

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 around the waist, placed it in a convenient pocket).

Give consideration to whether the nature of the process is likely to result in a significant difference between the actual exposure of the worker and the concentration of 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

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 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. Measure the atmospheric temperature and pressure at the start of the sampling period (see 9.1.3) using the thermometer and barometer, 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), it is possible the volumetric flow rate will change and 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, and record the measured value. Measure the atmospheric temperature and pressure at the end of the sampling period (see 9.1.3) using the thermometer and barometer, 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, 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.

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

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

9.5 Transportation

9.5.1 Samplers that collect airborne particles on the filter

For samplers that collect airborne particles on the filter (see NOTE 2 to 7.1.1), remove the filter from each sampler, place in a labelled filter transport cassette (7.1.5) 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.

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

9.5.2 Samplers with an internal filter cassette

For samplers with an internal filter cassette (see NOTE 2 to 7.1.1), except when using quartz fibre filters (see 9.5.1), 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 of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

In the cases described in 9.5.2 and 9.5.3 when using quartz fibre filters, place the filter in a screw-cap polyethylene vessel immediately after sampling using clean PTFE tweezers, rinse the internal surfaces of the filter cassette into the sample vessel with 4,0 ml of extraction solution, close with a plastic cap and shake gently.

It is possible to carry out the extraction in the samplers described in 9.5.2 and 9.5.3 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.

NOTE Anecdotal evidence[19] suggests that it is necessary to extract sulfate from quartz fibre filters immediately after sampling to achieve quantitative recovery of sulfuric acid.

9.5.4 Transport of samples to the laboratory

Transport the samples (see 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.

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

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, 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 sulfuric acid or phosphoric acid.

10.1.2 Quartz fibre filters

Swirl each screw-cap polyethylene vessel or sampling cassette (see 9.5.3) to mix the contents, ensuring that the filter remains completely immersed. Agitate for 15 min in an ultrasonic bath and then allow the immersed filters to sit for 1 h at room temperature, swirling or agitating occasionally.

If the extraction is to be carried out in a sampler of the disposable cassette type (see 9.5.3), the protective plug should be removed from the sample inlet orifice and the sampler should be maintained in an upright position while in the ultrasonic bath to avoid spillage and contamination of the sample solution.

Filter each sample solution through a membrane filter (7.2.4) using a disposable syringe, dispensing each filtrate into an individual, labelled, autosampler vial.

10.1.3 PVC and PTFE filters

Open the filter transport cassettes, sampler filter cassettes or samplers (see 9.5) and transfer each filter into an individual, labelled 50 ml beaker using clean PTFE tweezers, ensuring that the side of the filter on which the sample was collected is facing upwards. A disposable tube can also be used for the extraction, ensuring that the filter is immersed when the extraction solution is added. 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 should be added to the sampler via the air inlet orifice and the samplers should be maintained in an upright position while in the ultrasonic bath to avoid spillage and contamination of the sample solutions.

Accurately pipette 4,0 ml of extraction solution into each beaker or disposable tube. 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.

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

Filter each sample solution through a membrane filter (7.2.4), e.g. by using a disposable syringe, dispensing each filtrate into an individual, labelled, autosampler vial.

10.1.4 Preparation of calibration solutions

A multi-point (the number of points to be consistent with the quality system of the laboratory) calibration shall be constructed within the linear range of the analytical method to cover a proper concentration range of sulfate and phosphate. Accurately pipette appropriate volumes of sulfate and phosphate working standard solution (6.6) into individual, labelled one-mark volumetric flasks, dilute to the mark with water (6.1) or eluent (6.5), stopper and mix thoroughly. Prepare these calibration solutions fresh daily.

10.2 Instrumental analysis

Inject the calibration solutions (see 10.1.4) 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.

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

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

Inject the laboratory blank solutions (see 10.4.1) and the blank and sample test solutions (see 10.1) into the ion chromatography system and make conductivity measurements for each solution. Use the stored calibration function to determine the concentration, in milligrams per litre, of sulfuric acid or phosphoric acid.

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:

- use the instrument software to correct for the sensitivity change (reslope facility);
- 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 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) when making dilutions, so that the diluted test solutions and the calibration solutions are matrix-matched, and record the dilution factor, f_{dilution}.

NOTE 2 For samples expected to have very high concentrations of sulfate or phosphate, it can be necessary to dilute the test solutions before they are first analysed.

10.3 Estimation of detection and quantification limits

10.3.1 Estimation of the instrumental detection limits

Estimate the instrumental detection limits for sulfate and phosphate under the working analytical conditions, following the described procedure, 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[20]. 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.

Prepare a test solution with sulfate and phosphate concentrations near the anticipated instrumental detection limits, by diluting the working standard solution by an appropriate factor. Make at least 10 ion chromatographic measurements on the test solution (10 separately created test solutions) 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

Estimate the method detection limit and quantification limit under the working analytical conditions following the procedure described in 10.3.1 (which is based upon the approach described in Reference [20]) and repeat this exercise whenever the experimental conditions are changed significantly.

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 by an appropriate factor. Make ion chromatographic measurements on the test solutions derived from each spiked filter, after carrying out extraction of the filters, and calculate the method detection limit and the quantification limit as three times and ten times the sample standard deviation of the mean concentration value, respectively.

NOTE An alternative procedure for estimating the instrumental detection limit involves the analysis of filter samples fortified with the analyte of interest at values spanning the predicted detection limit[20].

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 according to 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 recur.

10.4.2 Quality control solutions

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.

Monitor the performance of the method by plotting control charts of the relative percentage recoveries and of the relative percentage differences between the spiked samples and the spiked duplicate samples. If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action, and reanalyse the samples if necessary. See ASTM E882[7] for general guidance on the use of quality control charts.

10.4.3 Certified reference materials

Suitable 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)[18] or a national accreditation organization.

10.5 Measurement uncertainty

It is recommended that laboratories estimate and report the uncertainty of their measurements in accordance with ISO/IEC Guide 98-3:2008[4]. The first step is to construct a cause and effect diagram[16] to identify the individual sources of random and systematic error in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of two is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 References [16] and [17] 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, 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 Formula (2):

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

where

$\rho_{\mathrm{anion,0}}$	is the mean concentration, in milligrams per litre, of sulfate or phosphate in the field blank test solutions;
$\rho_{\mathrm{anion,1}}$	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 $f_{\mathrm{dilution}} = 1$);
$f_{\mathrm{conversion}}$	is the factor to convert from anion to acid concentration ($f_{\mathrm{conversion}}$ = 1,021 for sulfate; $f_{\mathrm{conversion}}$ = 1,0318 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[12], 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[15].

12.2 Quantification limits

The target values for quantification limits depend on the applicable local limit value. In accordance with ISO 20581[3], 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.

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[15] 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.

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[15] to be in the range 97 % to 100 % for both phosphoric acid and sulfuric acid.

12.4.2 Analytical precision

The component of the coefficient of variation of the method that arises from analytical variability, $CV_{analysis}$, determined from the analysis of spiked filters, has been found[15] to be in the range 0,7 % to 3,2 % for phosphoric acid and 0,5 % to 2,6 % for sulfuric acid.

12.5 Uncertainty of sampling and analysis method

The expanded uncertainty of the method, using a coverage factor of two, has been estimated to be < 23 % for both phosphoric acid and sulfuric acid.

12.6 Interferences

The ubiquitous presence of sulfate and phosphate leads to blank values being produced by the reagents and equipment used in the method (chemicals, glassware). Therefore, the blank values of all chemicals and equipment have to be carefully checked.

Both sulfate and phosphate are found ubiquitously in the environment. The procedure does not allow differentiation between anions found ubiquitously and those due to the presence of the free acids in workplace air (see 9.1.5). In work areas where no distinction can be made between sulfuric or phosphoric acid aerosols and aerosols containing sulfate or phosphate, a sample also needs to be taken of the emission source (e.g. pickling bath solution) in parallel with the air samples (see 9.1.5). Both the free sulfuric or phosphoric acid and the total phosphate or sulfate content of the emission source sample should be determined[21].

A correction factor for air concentration, *K*, is calculated from the results of the analysis of the emission source sample, using Formula (3):

$$K = \frac{\rho_{\text{acid}}}{\rho_{\text{anion}}} \tag{3}$$

where

ρ_{acid} is the sulfuric or phosphoric acid concentration of the emission source sample, determined by acid-base titration;

ρ_{anion} is the sulfate or phosphate concentration of the emission source sample (calculated as sulfuric or phosphoric acid), determined by ion chromatography.

Measurements of the mass concentration of sulfuric acid or phosphoric acid in the air samples are then corrected by the factor calculated. Formula (4) yields the corrected concentration, $\rho_{\text{acid,corr}}$, in milligrams per cubic metre, of sulfuric or phosphoric acid in the air sample:

$$\rho_{\text{acid,corr}} = K \times \rho_{\text{acid,det}} \tag{4}$$

where $\rho_{\text{acid,det}}$ is the determined concentration, in milligrams per cubic metre, of sulfuric or phosphoric acid in the air sample (see Clause 11).

NOTE Diphosphorus pentoxide (P_2O_5) reacts with water to form phosphoric acid, and the two substances therefore cannot be differentiated.

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) a complete identification of the air sample, including the date of sampling, the place of sampling, the type of sample (personal or static), either the identity of the individual whose breathing zone was sampled (or other personal identifier) or the location at which the general occupational environment was sampled (for a static sample), a 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 21438-1;

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

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

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

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

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

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

m) the time-weighted average mass concentration, in milligrams per cubic metre, of sulfuric acid or phosphoric acid found in the air sample 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 sulfate and phosphate 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 sulfuric acid or phosphoric acid per filter sample.

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

p) the estimated instrumental detection limits, method detection limits and quantification limits under the working analytical conditions; the measurement uncertainty determined in accordance with ISO/IEC Guide 98-3:2008[4] 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 date of the analysis;

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

13.2 Laboratory report

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