INTERNATIONAL STANDARD

ISO 21438-1

Second edition
2022-05

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
ISO 21438-1:2022(E)

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

Published in Switzerland

Contents

Foreword

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

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO 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.

INTERNATIONAL STANDARD ISO 21438-1:2022(E)

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.