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Workplace air — Determination of arsenic and arsenic compounds by electrothermal atomic absorption spectrometry —

Part 1: Arsenic and arsenic compounds, except arsine by ET-AAS

Air des lieux de travail — Détermination de l'arsenic et des composés d'arsenic par spectrométrie d'absorption atomique avec atomisation électrothermique —

Partie 1: Arsenic et composés d'arsenic, à l'exception de l'arsine par ET-AAS

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Foreword

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

A list of all parts in the ISO 6323 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

Arsenic and arsenic compounds are toxic and are recognized as human carcinogens. In particular arsenic and arsenic compounds are a hazard to the health of workers in many industries through exposure by inhalation. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure. The collection of samples of air during a work activity and then measuring the amount of particular arsenic and arsenic compounds are often done to assess an individual's exposure, the effectiveness of workplace controls or respiratory protection measures. The air sampling can be done as stationary or personal air sampling. Electrothermal atomic absorption spectrometry (ET-AAS) analysis of particular arsenic and arsenic compounds in a sample of respirable or inhalable dust collected on a collection substrate (membrane filter) is employed in many countries to measure and estimate exposure to arsenic and arsenic compounds. ET-AAS is able to quantify arsenic and arsenic compounds.

Workplace air — Determination of arsenic and arsenic compounds by electrothermal atomic absorption spectrometry —

Part 1:
Arsenic and arsenic compounds, except arsine by ET-AAS

1 Scope

This document specifies a method for the determination of the mass concentration of particulate arsenic and arsenic compounds in workplace air sampled on a filter (e. g. 37 mm cellulose nitrate filter), digested with acid or an acid mixture and analysed quantitively by using electrothermal atomic absorption spectrometry (ET-AAS). The method is not suitable for determination of arsenic in the form of metal arsenides, which decompose in the presence of water or acid, or for arsenic trioxide vapour.

Many different types of sampling apparatus are used to collect respirable or inhalable dust, according to the occupational hygiene convention. This document is designed to accommodate the variety of samplers and collection substrates available to analysts. This document is intended to be used in conjunction with ISO 21832 which promotes best practices for these analyses.

The method is applicable to the determination of masses of approximately 0,2 µg to 2 µg of arsenic per sample, for analysis of test solutions prepared using sample solution aliquots in the recommended range (see 10.1.3 and 10.1.4.1). The concentration range for arsenic in air, for which this procedure is applicable, is determined in part by the sampling procedure selected by the user.

The method is applicable to personal and stationary air sampling.

A number of transition metals can interfere with the determination of arsenic by electrothermal atomic absorption spectrometry (see 11.3).

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

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

ISO 13137, *Workplace atmospheres — Pumps for personal sampling of chemical and biological agents — Requirements and test methods*

ISO 18158, *Workplace air — Terminology*

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

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

DIN 12353, *Laboratory ware made from fused quartz and fused silica; boiling flasks made from fused quartz; round bottom flasks, flat bottom flasks and conical flasks*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158 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/

4 Principle

A filter (6.2.1; see Table 1) is mounted in a sampler (6.1.1) designed to collect the respirable or inhalable fraction of airborne particles. The sampling can be performed with personal or stationary fixed samplers. Before sampling is performed, the filter batch used shall be verified with regard to its metal content and consequently the suitability of the minimum requirements for the performance of measuring methods.

Currently limit values in different countries exist for arsenic and its compounds either as "total dust", defined by the performance of a sampler, or in the inhalable size selective fraction. A suitable sampling device for the applicable particle fraction shall be used considering the existing limit value/particle fraction.

The fraction separated on the filter is analysed for arsenic after acid digestion using ET-AAS. As digestion media, nitric acid or a mixture of nitric and hydrochloric acid can be used. The sample solution is allowed to cool and diluted to a given volume with ultrapure water (7.3.1), depending on the digestion type used. A test solution is prepared by transferring an aliquot of the sample solution to a volumetric flask and dilution to volume with ultrapure water.

The atomic absorption spectrometer is equipped with an arsenic hollow cathode lamp or electrodeless charge lamp and heated electrically.

Absorbance measurements are made at 193,7 nm or 197,2 nm, using a graphite furnace with platform and a matrix modifier (7.4.1.2). For background compensation, Zeeman-Mode is used. Deuterium background compensation can also be used as an option. Results obtained by the analytical-curve technique or the analyte addition technique.

5 Requirement

The measuring procedure shall conform to ISO 20581 or ISO 21832, which specify performance requirements for procedures for measuring chemical agents in workplace air.

6 Apparatus and equipment

6.1 Sampling equipment

6.1.1 Sampler

The performance of the sampler used shall match the criteria for respirable or inhalable dust as specified in ISO 7708. Samplers that use 37 mm diameter filters (6.2.1) as the collection substrate are required. A plastic filter capsule for filters with a diameter of 37 mm are necessary. A suitable supporting grid can be necessary.

Each sampler should be labelled with a unique number, in order to identify samplers that start to under-perform after long-term use.

Samplers shall meet the manufacturer's requirements for calibration.

NOTE 1 For person-related or stationary sampling, filters with diameters of e.g. 70 mm up to 150 mm, can also be used with specific sampling systems, with appropriate adjustments to the digestion conditions.

NOTE 2 In some countries, there can be exceptions due to national requirements.

6.1.2 Filter capsule

Matching plastic filter capsule with covers for the 37 mm filter (6.2.1), for insertion into the sampler.

6.1.3 Sampling pumps

Sampling pumps shall conform to the requirements of ISO 13137.

If the sampling pump is used outside the range of conditions specified in ISO 13137, appropriate actions should be taken to ensure that the performance requirements are met.

6.1.4 Portable flowmeter

The flowmeter shall conform to the requirements of ISO 13137.

The flowmeter shall be capable of measuring the appropriate flow rate (see 9.3.1 and 9.4) to within ±5 %, and calibrated against a primary standard, i.e. a flowmeter of which the accuracy is traceable to national standards. If appropriate, the atmospheric temperature and pressure at which the flowmeter was calibrated should be recorded.

6.1.5 Silicone adapter

The silicone adapter shall fit into the sampler head to connect the flowmeter (6.1.4) for measuring/setting the air flow.

6.1.6 Ancillary equipment

The following ancillary equipment shall be used:

a) flexible tubing, to connect the sampler to the sampling pump (6.1.3);

b) belts or harnesses to which the sampling pumps can conveniently be fixed for personal air sampling; a tripod is required for person-related or stationary sampling;

c) a means to transport the samples from the workplace to the laboratory, which minimises the possibility of accidental transfers of collected dust to or from the collection substrate (filter); transportation requires caps or covers for the samplers (filter capsule);

d) a thermometer (readable to 1 °C) and a barometer (readable to 0,1 kPa), to measure atmospheric temperature and pressure for flow rate correction, when the temperature and pressure at the time of use differ from the conditions under which the flowmeter (6.1.4) was calibrated.

6.2 Collection media

6.2.1 Filters

Filters shall be of a diameter suitable for use in the selected sampler (6.1.1) and have a capture efficiency for respirable or inhalable particles of not less than 99 %. It is important for the analyst to know the composition of the collection substrate used to collect the sample since it has a direct bearing on the analytical approach used. The collection substrates generally used for the sampling of arsenic and arsenic compounds, and their characteristics, are listed in Table 1.

Table 1 — Dust collection substrates

Sampling medium (pore size)	Comments
Cellulose nitrate/cellulose acetate membrane filters (8 µm)	Membrane filters are very suitable for subsequent analysis of metals in dust, as they exhibit very low blank values and can be readily digested by acids.
Mixed esters of cellulose (MCE) (0,8 µm)	MCE filters are comprised mixtures of cellulose acetate and cellulose nitrate. They are low in in metal background and completely dissolvable with acids.
Quartz glass fibre filters	They are suitable for dust sampling due to their good retention capacity. As a result of their exceedingly low and relatively constant blank values, they are substantially more suitable than glass fibre filters for the screening of dusts for metallic components.
Glass fibre filters	The high and often fluctuating blank values of this filter material can adversely affect the analysis of metals in dust.
Fluoropolymer filters (PTFE)	They exhibit high chemical and thermal durability and are not dissolved by common digestion agents. Their blank value concentrations are low, however, this filter material must be tested before use, as it can contain small amounts of metals. Furthermore, the high flow resistance of this filter material must be taken into consideration.
Other filter materials Polycarbonate or polyvinyl chloride filters (PVC)	Other filter materials can also be used such as polycarbonate or polyvinyl chloride (PVC) filters. Polycarbonate filters, in particular, have a very good resistance to chemicals.
Polyurethane foams	Polyurethane foams (PU foams) can be manufactured with various pore sizes and are suitable for dividing collections of particles into fractions. Depending on the manufacturing process, PU foams can contain many interfering impurities due to auxiliary components (e.g. organic tin compounds), pre-cleaning of the material is crucial to minimise blank values. The limited solubility of the material during digestion can also lead to interference.
Disposable inhalable sampler (DIS) with filter or foam and filter	DIS is a single-use sampler for the inhalable fraction and includes an MCE filter bonded to a cellulose capsule. If the capsule is fitted with a foam pre-selector, the analysis of the capsule corresponds to the respirable fraction. The inhalable fraction is the sum of the pre-selector foam and the capsule bonded with MCE filter. Effects of wall deposits can be eliminated with this sampler type.

Cellulose membrane filters are rigid and easy to handle when weighing and loading the sampler. Glass fibre filters, quartz glass fibre filters, PVC and especially polycarbonate filters are flexible and require careful handling.

NOTE Cellulose membrane filters completely dissolve when digested with nitric and hydrochloric acid, or only nitric acid. Glass or quartz fibre filters, PVC or polycarbonate filters do not completely dissolve in digestion media hydrochloric and or nitric acid. It can be necessary to filter the digestion solution before analysis.

6.2.2 Recommendations for filters

An important property of an analytical filter (6.2.1) is that it should contain no or only low concentrations of the metals to be analysed. A constantly stable concentration of metal content of the filter is also easy to handle. Filter materials listed in Table 1 generally do not contain compounds that interfere with the measurement of arsenic and arsenic compounds. Impurities can be introduced during the filter manufacturing process and blank values can increase depending on filter material. Therefore, batches of filters should be regularly tested to detect potential interferences and background levels.

It is advisable to use filters that exhibit no blank values or blank values that are as low as possible and constant. Experience has shown that blank value concentrations are batch-dependent, therefore a test

certificate giving information on relevant components of the filters should be available (e.g. from the manufacturer or supplier). The test certificate should contain information on the level of the metal content and their bandwidth. Only filters from a single batch should be used in the course of a measurement series. Cellulose nitrate membrane filters exhibit the least variability and lowest background levels and thus are useful in situations where low limits of detection are required.

6.2.3 Back pressure of filters

Some filters (6.2.1) have a high back pressure and thereby negatively influence the sampling, due to a higher load on the pump. High values for back pressure can compromise the sampling time, when the sampling of a complete 8 h shift is desired.

6.2.4 Weighing of filters

Weighing can be performed to determine the inhalable or respirable fraction and should be performed following ISO 15767[1] (see 9.2.4). Filters (6.2.1) shall not be weighed in cassettes as large weight variations have been reported.[2] Reference shall be made to the instructions of the collection substrate manufacturer.

6.3 Equipment for the determination of dust concentration

If the determination of the inhalable or respirable fraction should be performed, a microbalance capable of weighing ±1 µg or better over the range 0 g to 5 g is required. An electrostatic eliminator is needed when weighing collection substrates. Weighing should be performed according to ISO 15767[1].

6.4 Equipment for sample digestion

6.4.1 General

Equipment and aids for the digestion of metals and metal compounds in dust samples are listed in 6.4.2 to 6.4.4. All equipment and materials used should be as metal-free as possible. Inert materials should be used for digestion. Contamination with metals by equipment or materials used shall be avoided. If necessary, the equipment should be suitable cleaned before use.

6.4.2 Equipment for all types of sample digestion

6.4.2.1 Ceramic tweezer, for the transfer of the filters (6.2.1) into the digestion vessels.

6.4.2.2 Measuring cylinder of perfluoralkoxy-alkane (PFA) copolymer with volumes of 50 ml, 100 ml and 500 ml.

6.4.2.3 Quartz glass bottle with a polytetrafluorethylene (PTFE) dispenser for the transfer of the digestion acid or acid mixture into the digestion vessels.

6.4.2.4 Bottle of PFA with PTFE dispenser, for adding ultrapure water (7.3.1) to the digested samples.

6.4.3 Laboratory equipment for open vessel hot block digestion

6.4.3.1 Heating block made of metal or graphite with time/temperature control.

6.4.3.2 Graduated digestion vessels, preferably made of quartz glass or of comparable quality in accordance with the requirements of DIN 12353 for reaction vessels.

Vessels made of borosilicate glass should not be used due to possible interference from boron.

6.4.3.3 Air cooler, preferably made of quartz glass with standard inner and outer ground glass joints for mounting on a digestion vessel or of comparable quality in accordance with the requirements of ISO 1042 and DIN 12353.

6.4.3.4 Boiling rods, preferably made of quartz glass with replaceable endpieces (e.g. PTFE tube).

6.4.3.5 Polyethylene plugs for digestion vessels.

6.4.4 Laboratory equipment for high pressure microwave digestion

6.4.4.1 High pressure microwave digestion system

6.4.4.2 Suitable digestion vessels for the microwave, for instance made of quartz glass or PTFE.

6.5 Equipment for analysis

6.5.1 General

Equipment for the quantitative determination of metals and metal compounds in dust samples are listed in 6.5.2 and 6.5.3. All equipment and materials used should be as metal-free as possible. Inert materials should be used for digestion. Contamination with metals by equipment or materials used shall be reduced to a minimum. If necessary, the equipment should be suitably cleaned before use.

6.5.2 Equipment for sample preparation

6.5.2.1 Volumetric flasks of PFA for standard and calibration solutions, with screw cap and ring mark, volumes of 5 ml, 10 ml, 50 ml, 100 ml, 500 ml, 1 000 ml.

6.5.2.2 Various adjustable piston pipettes for covering a volume range of 2 µl to 10 ml.

6.5.2.3 Disposable polysytrol vessels with a volume of approximately 1,5 ml for the autosampler.

6.5.2.4 Electronic precision balance, for weighing the calibration standards.

6.5.2.5 Ultrapure water system with reverse osmosis system and ultrapure water system, for the preparation of ultrapure water (resistivity greater than 18,2 MΩ · cm at 25 °C).

6.5.3 Analytical system

Electrothermal atomic absorption spectrometer (ET-AAS), preferably with Zeeman background correction and autosampler, graphite tube with platform, pyrocoated and arsenic hollow cathode lamp. As an alternative, deuterium background compensation can also be used.

7 Reagents

7.1 General

Use only reagents of recognised analytical grade and only water as specified in 7.3.1. It is advisable to check the blank values of chemicals before use. Only batch-related chemicals should be used for digestion. Furthermore, the chemicals used shall be as free of metals as possible. The content of the analytical standards for calibration and quality assurance shall be traceable to standard reference materials.

7.2 Water

Use water from a purification system that delivers ultrapure water of grade 1 as defined in ISO 3696.

NOTE State of the art water purification systems deliver water of grade 1 with higher quality than specified in ISO 3696 (e.g. resistivity greater than 18,2 MΩ · cm at 25 °C).

7.3 Chemicals for digestion

7.3.1 Ultrapure water, (ρ ≥ 18,2 MΩ · cm at 25 °C), low metal content and an especially low content of boron and alkalis.

7.3.2 Nitric acid 65 %; low metal content.

7.3.3 Hydrochloric acid 25 %; low metal content.

7.4 Chemicals for analysis

7.4.1 Stabilization and modifier

7.4.1.1 Nitric acid 67 % - 70 %; low metal content, for stabilization of calibration and quality control standards. A stabilization solution of approx. 0,7 % nitric acid is produced by diluting the concentrated nitric acid with ultrapure water 1+9 in a volumetric flask.

7.4.1.2 Matrix modifier e.g. nickel 1 000 mg/l, traceable to national standards.

7.4.2 Calibration and quality control standards

7.4.2.1 Arsenic plasma standard, e.g. 1 000 mg/l, traceable to national standards, for calibration standards.

7.4.2.2 Multielement quality control standard with arsenic, e.g. 1 000 mg/l, traceable to national standards.

7.4.2.3 Gas for analytical system, e.g., ultra-high purity argon (grade 5.0), minimum purity 99,999 %.

7.5 Chemicals for method validation

7.5.1 Arsenic (III)oxide, 99,996 % (metals basis excluding Sb), max. 20 ppm Sb, powder.

7.5.2 Arsenic (III)iodide, 99,999 % (metals basis), 80 mesh powder.

8 Occupational exposure assessment

Refer to relevant standards, e.g. ISO 20581, EN 689[3] or ASTM E1370[3] 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 Collection characteristics and flow rate

Select samplers (6.1.1) suitable for collection of the applicable fraction of airborne particles according to the existing 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 ISO 13137.

Use the samplers at their design flow rate and in accordance with the instructions provided by the manufacturer.

The flow rate of the sampler used shall be selected in such a way that, depending on the sampling duration, the requirements for a measurement procedure can be achieved in relation to the existing limit value.

9.1.2 Sampling period

Select a sampling period of appropriate duration, using any available information about the work process and test atmosphere, so that the amount of arsenic is within the recommended working range of the method. When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the filter (6.2.1) 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 arsenic and arsenic compounds is present in the test atmosphere at a concentration of defined times (see ISO 21832) its limit value, using Formula (1):

$$t_{min} = \frac{m_{lower}}{q_V \times x \times \rho_{LV}} \quad (1)$$

where

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

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

x is the factor to ensure the requirements of a measurement procedure for a limit value (e.g. 0,1 times);

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

NOTE If the minimum sampling time is not long enough for the method to be useful for the intended measurement task, a sampler designed to be used at a higher flow rate can be considered.

9.1.3 Temperature and pressure effects

Refer to the manufacturer's instructions to determine whether the indicated volumetric flow rate of the flowmeter (6.1.4) is dependent upon temperature and pressure. Consider if it is necessary to make a correction to take into account any difference between the atmospheric temperature and pressure at the time of calibration of the flowmeter and at the time of sampling. Make a correction if it is considered possible that an error of greater than ±5 % will be introduced. If a correction is to be made, measure and record the atmospheric temperature and pressure at the start and the end of the sampling period (see 9.5.1 and 9.5.3).

NOTE An example of temperature and pressure correction for the indicated flow rate is given in Annex A for a flowmeter of variable area with constant pressure drop.

9.1.4 Sample handling

To minimise the risk of damage or contamination, only handle filters (6.2.1) in a clean area where the concentration of arsenic and arsenic compounds in air and atmosphere is minimal as usual. Handle filters only with ceramic tweezers (6.4.2.1).

9.2 Sample preparation

9.2.1 Cleaning

Reusable equipment, e.g. filter capsules (6.1.2) and covers, shall be cleaned before use to prevent contamination of previous work. Dismantle the parts, soak the samplers (6.1.1) in detergent, ultrasound to remove the fine dust and rinse in ultrapure water (7.3.1). As an alternative a cleaning procedure in a laboratory automatic washer (with acid rinse cycle) can be used. Allow time the apparatus to dry before reassembly.

9.2.2 Filter

The filter (6.2.1) shall be placed with ceramic tweezers (6.4.2.1) in the filter capsule (6.1.2), fixed and sealed for transportation with the covers.

9.2.3 Marking

The samplers used should be marked unambiguously in order to prevent confusion with other samplers.

9.2.4 Pre-weighing of filters

If required for the determination of inhalable or respirable fraction, pre-weighing of filters (6.2.1) is necessary. Pre-weigh each uniquely identified collection media (including a minimum of three blanks) using flat tipped ceramic tweezers (6.4.2.1) to avoid contamination and damage at least to the nearest 0,01 mg, according to ISO 15767[1].

9.2.5 Assembly

The covers of the filter capsule (6.1.2) must be moved before the capsule can be placed into the sampler. Connect each loaded sampler to a sampling pump (6.1.3) and test for leaks.

9.3 Sampling preparation

9.3.1 Initial flow rate

Perform the following in a clean area, where the concentration of arsenic and arsenic compounds is minimal.

Connect the sampler (6.1.1) with flexible tubes to the sampling pump (6.1.3) and adjust the flow rate to within a maximum deviation of ±5 % of the required value. The flow rate shall be recorded. 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.

9.3.2 Field blanks

Retain as field blanks, one unused loaded sampler (6.1.1) from each batch of 10 prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters (6.2.1).

9.3.3 Personal sampling

Position the sampler (6.1.1) 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 (6.1.3) to the worker in a manner that causes minimum inconvenience, e.g. to a belt around the waist, or place 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 arsenic and arsenic compounds 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.

NOTE The breathing zone has been defined in ISO 18158 or EN 1540[5] as the space around worker`s nose and mouth from which breath is taken. Technically, the breathing zone corresponds to a hemisphere (generally accepted to be 30 cm in radius) extending in front of the human face, centred on the midpoint 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. This technical description is not applicable when respiratory protective equipment is used.

9.3.4 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 characterise the background level of arsenic and arsenic compounds in the workplace, select a sampling position that is sufficiently remote from the work processes, such that results will not be directly affected by arsenic and arsenic compounds from emission sources.

9.4 Parameters

The method described in this document was validated with the parameters for a GSP-10 sampler listed in Table 2.

Table 2 — Parameters for a GSP-10 sampler

Parameter	Value
Sampling duration	Minimum 2 h, up to 8 h
Flow rate	10 l/min
Temperature	At room temperature, 20 °C to 24 °C

NOTE The humidity does not exert an influence. The influence of higher or lower temperatures was not tested.

If another sampler is used, the parameters shall be set in accordance with the requirements of ISO 7708.

9.5 Performing the sampling

9.5.1 Start of the sampling period

When ready to begin sampling, remove the protective cover or plug from the sampler (6.1.1) and switch on the sampling pump (6.1.3). 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 (6.1.6), and record the measured values.

Taking into account the limit of quantification of arsenic and arsenic compounds with ET-AAS and the flow rate of the sampling system, a minimum sampling time of 2 h is needed so that compliance with the occupational exposure limit value (OELV) can be reliably assessed.

9.5.2 Sampling period

Since it its possible for a filter (6.2.1) to become clogged, monitor the performance of the sampler frequently, minimum of once per hour.

NOTE Regular observation of the flow-fault indicator is an acceptable means of assuring that the flow rate of the flow-stabilized sampling pump is maintained satisfactorily, provided that the flow-fault indicator indicates malfunction when the flow rate is outside ±5 % of the nominal value.

9.5.3 End of the sampling period

At the end of the sampling period switch off the pump (6.1.3), record the time and verify the volumetric flow rate to the sampler according to 9.3.1. 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 (6.1.4), 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 (6.1.6), and record the measured values.

Record the relevant details of the sample collection. Details needed by the laboratory analyst are the following:

a) type of sampler used to collect the sample;

b) type of collection material;

c) unique identifier of each sample;

d) volume of the air sampled, calculated in accordance with ISO 13137;

e) information about the industrial process that can influence evaluation of results.

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

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

Calculate the volume of air sampled, in litres, at atmospheric temperature and pressure, by multiplying the mean flow rate, in litres per minute, by the sampling time, in minutes.

9.6 Transport and storage

9.6.1 General

Perform the transport and storage in an area where arsenic and arsenic compounds is known to be low.

9.6.2 Transportation

The loaded and labelled samplers (6.1.1) in the filter capsules (6.1.2) shall be removed from each sampler and sealed with the covers for transportation to the laboratory. The transport should be as vibration-free as possible in a container which has been designed to prevent damage to the samples in transit, and which has been labelled to assure proper handling.

9.6.3 Storage

In the laboratory, the sealed samplers (6.1.1) can be stored at room temperature and normal humidity. Losses of sample can occur, if pressure is applied to the surface of the dust collected on a filter (6.2.1), especially during the transfer of the filter from a filter capsule. For example, sample losses can occur if the sample surface comes into contact with tweezers (6.4.2.1) or the edge of the sampler.

Filters can become charged during sampling and can attract themselves to these items. Losses of dust from the filter surface or found in the capsule shall be noted on the report.

10 Analysis

CAUTION — Use suitable personal protective equipment (including gloves, face shield or safety glasses, etc.) while carrying out the analysis.

10.1 Preparation

10.1.1 General

Before use, clean all glassware and plastic bottles to remove any residual grease or chemicals with diluted nitric acid and then with ultrapure water (7.3.1). Allow time to dry before use. Alternatively, a laboratory automatic washer (with acid rinse cycle) can be used.

10.1.2 Weighing

If required to determine the inhalable or respirable fraction the filters (6.2.1) have to be conditioned for at least 24 h in defined temperature and humidity. Therefore, the covers of the capsules have to be opened. For weighing after conditioning the filters, a flat tipped ceramic tweezers shall be used.

After the filters have been weighed, they shall be placed in the correct filter capsule and sealed.

10.1.3 Digestion

10.1.3.1 General

For determining arsenic and arsenic compounds in dust at workplaces, use one of the following digestion methods. Other digestion methods can be used if verified to provide equivalent performance.

10.1.3.2 Open hot-block digestion

Remove the filter (6.2.1) from the filter capsule with clean and flat-tipped ceramic tweezers (6.4.2.1) and transfer it to the digestion vessel (6.4.3.2). Use the equipment mentioned in 6.4. Then the filter is covered with 10 ml of digestion agent (2 parts by volume of nitric acid ≥65 % (7.3.2), and 1 part by volume of hydrochloric acid 25 % (7.3.3), mixed before in quartz glass bottle (6.4.2.3)). It is important to ensure that the loaded filter is completely immersed in the digestion agent. The digestion vessel is equipped with a boiling rod and an air cooler (approx. 40 cm long) and is subsequently kept in a thermostatically controlled heating block (6.4.3.1) with suitable bore holes for 2 h under reflux (block temperature approx. 125 °C).

After cooling, 10 ml ultrapure water (7.3.1) is cautiously added to the digestion vessel through the cooler and heating is repeated. After cooling again, the volume of the sample digestion solution is read off. Alternatively, after heating for 2 h, the sample digestion solution can be transferred to a suitable volumetric flask (e.g. a 20 mL volumetric flask), rinsed with ultrapure water if necessary and then the flask is filled to the mark with ultrapure water. The sample solution is then homogenised once again. As a rule, a further dilution step is required before analysis. The degree of dilution depends on the analytical procedure used and on the selected method of measurement.

10.1.3.3 High-pressure microwave digestion

Microwave assisted pressure digestion can be carried out as an alternative to open digestion methods. This procedure involves a closed system, in which the temperature and time can be varied.

The loaded filter (6.2.1) is transferred into the digestion vessel. Then 10 ml of the digestion agent (nitric acid ≥65 %, 7.3.2) is added to the filter. The digestion can be carried out at 1 100 W, at a maximum temperature of 240 °C for 1 h. After digestion, the sample is transferred in its entirety to a suitable volumetric flask (e.g. 25 ml) and the flask is filled to the mark with ultrapure water (7.3.1). The sample is filtered and diluted if necessary and then transferred to the analytical instrument. The degree of dilution depends on the analytical technique used and on the selected measurement method.

NOTE Similar high-pressure microwave programs that have been checked for their suitability can also be used.

10.1.4 Solutions

10.1.4.1 Sample and blank test solutions

Prepare sample and blank test solutions for analysis. A minimum dilution of 1:4 is necessary. Therefore, transfer an aliquot of the digested solution in a volumetric flask, fill up with three parts of 0,7 % nitric acid (7.4.1.1) in a volumetric flask, stopper and mix thoroughly.

A minimum of two blank test solutions shall be analysed each analysis run.

A higher dilution is required if the arsenic concentration is outside the analytical measuring range. The blank test solutions shall be diluted in the same way.

10.1.4.2 Calibration solutions

A multi-point calibration shall be constructed within the linear range of the analytical method to cover a proper concentration range of arsenic. The number of points should be consistent with the quality system of the laboratory. Accurately pipette appropriate volumes of arsenic plasma standard solution (7.4.2.1) into individual, labelled one-mark volumetric flasks, dilute to the mark with 0,7 % nitric acid (7.4.1.1), stopper and mix thoroughly. A zero value for calibration is determined with 0,7 % nitric acid, stopper and mix thoroughly. A minimum of six additional calibration concentrations is recommended. Prepare calibration solutions fresh daily.

10.1.4.3 Quality control solutions

10.1.4.3.1 General

Prepare quality control solutions fresh daily.

10.1.4.3.2 Filter blanks

Carry filter blanks through the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. The filter blanks include the filter (6.2.1) and all reagents used for digestion and sample preparation. Prepare filter blank solutions in accordance to a frequency of at least one per 20 samples or a minimum of one per batch.

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

10.1.4.3.3 Arsenic quality control solutions

Quality control solutions are measured periodically to verify the measuring method. It is recommended to use a multielement quality control standard with arsenic (7.4.2.2). Perform two different solutions with an arsenic concentration in the lower and upper measuring range by diluting the standard solution with 0,7 % nitric acid in a volumetric flask, stopper and mix thoroughly.

10.2 Instrumental analysis

10.2.1 Set up the atomic absorption spectrometer (6.5.3) to make absorbance measurements at a specific arsenic wavelength. An analytical arsenic wavelength at 197,2 nm shall be used unless the highest sensitivity is required. The 193,7 nm arsenic wavelength is approximately twice as sensitive; its use is preferable because this wavelength offers a wider calibration range. Follow the manufacturer`s recommendations for specific parameters for the operation of instruments. Optimum concentrations of reagents and instrumental settings can vary according to the exact configuration of the system.

10.2.2 After a 15 min warm-up period for the lamp, inject the calibrations solutions (10.1.4.2), 20 µl and 5 µl matrix modifier (7.4.1.2), into the graphite furnace of the atomic absorption spectrometer in order of

increasing concentrations with the autosampler, and measure the absorbance of the arsenic peak for each calibration solution, in peak area mode. The dilution of the calibration solution is carried out automatically with 0,7 % nitric acid (7.4.1.1) via autosampler.

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

10.2.4 Inject the diluted filter blanks, field blanks and sample solutions (all with a primary dilution factor of four, see 10.1.4.1) into the graphite furnace of the atomic absorption spectrometer (6.5.3) with the autosampler and in addition of the matrix modifier. Make absorbance measurements for each solution. Use the stored calibration function to determine the concentration, in micrograms per litre, of arsenic.

10.2.5 Analyse the multielement quality control standards (10.1.4.3.2) with arsenic in two different concentrations after initial calibration, periodically after every 20 test solutions and at the end of measurement. The recovery of the quality standard must be within defined limits (±10 %); otherwise, the calibration shall be verified, and the analysis of the sample solutions repeated. The stability of the analytical instrument and the accuracy of the results are thereby checked.

10.2.6 If the concentrations of arsenic are above the upper limit of the linear calibration range, dilute the test solutions to bring them within the linear range, and repeat the analysis.

10.2.7 An electronic zero adjustment is made after each measurement. The zero value is regularly analysed by measuring a solution that does not contain arsenic (see 10.1.4.2) at the latest every 20 samples, and the signal (peak area) is set to zero. Afterwards, a complete recalibration is always carried out.

Typical operating parameters for determination of arsenic by electrothermal atomic absorption spectrometry are shown in Annex B.

10.3 Estimation of detection and quantification limits

10.3.1 Estimation of the instrumental detection limit

Estimate the instrumental detection limits for arsenic under the working analytical conditions following the procedure below and repeat this exercise whenever the experimental conditions are changed significantly.

NOTE An instrumental detection limit is of use in identifying changes in instrument performance, but it is not the same as a method limit of detection. An instrumental detection limit is likely to be lower than a method limit of detection 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 (ISO 21832).

Analyse the calibration blank solution at least ten times under repeatability conditions (10 separately created test solutions) and calculate the instrumental detection limits for arsenic as three times the sample standard deviation of the mean concentration values.

If there is no measurable response from the analytical instrument, prepare a test solution with concentrations of arsenic near their anticipated instrumental limits of detection by diluting the standard solutions by an appropriate factor. Analyse the test solution at least ten times under repeatability conditions (ISO 21832).

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 below and repeat this exercise whenever the experimental conditions are changed significantly.

For measuring procedures that involve sample dissolution, prepare at least 10 test solutions from laboratory blanks, following the sample preparation method described in the measuring procedure, and analyse the test solutions for arsenic under repeatability conditions (ISO 21832).

If there is no measurable response from the analytical instrument, spike 10 laboratory blanks with an appropriate volume of working standard solution containing appropriate known masses of arsenic, such that the test solutions produced from them will have concentrations near their respective anticipated limits of detection. Prepare test solutions from the spiked laboratory blanks, following the sample preparation method described in the measuring procedure, and analyse the test solutions for the metals or metalloids of interest under repeatability conditions (ISO 21832).

Calculate the method limit detection and the quantification limit for arsenic as three times and ten times the standard deviation of the mean concentration value, respectively.

10.4 Certified reference materials

Suitable certified reference materials (CRMs) for arsenic and arsenic compounds shall be analysed prior to routine use of the method to establish the analytical recovery of the method.

Use a suitable mass of the selected reference materials, taking into consideration the concentration of arsenic or arsenic compound in the reference material and the supplier's instructions on the minimum amount of material that is required for a homogenous sample.

It is preferable to use the smallest mass of reference material that can be easily weighed, to scale up the volume of reagents and to adjust the final test solution volume so that the experiment is as representative as possible of the analysis of workplace air samples.

10.5 Measurement uncertainty

It is recommended that laboratories estimate and report the uncertainty for measurement methods of chemical agents. Chemical agents in airborne particles involve the steps sampling and analysis for determine the measurement uncertainty, which are additionally divided into random and non-random errors.

ISO 21832:2018, Annex C contains an overview and an example for estimation of uncertainty measurements for metals/metalloids and their compounds.

Random and non-random uncertainty components for sampling contains typically (but not exclusive) the uncertainty associated with sampled air volume, sampling efficiency and sample storage and transportation.

Random and non-random uncertainty components for analysis contains typically (but not exclusive) the uncertainty associated with analytical recovery, analytical precision, calibration, dilution of sample solutions if applicable, instrument response drift and blank subtraction (see ISO 21832).

A coverage factor of 2 is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

11 Expression of results

11.1 Calculations

Calculate the mass concentration of arsenic in the air sample, ρ_{As}, in milligrams per cubic metre, at ambient conditions, using Formula (2):

$$\rho_{As} = \frac{\left(\rho_{As,1} \times V_1 \times F_1\right) - \left(\rho_{As,0} \times V_0 \times F_0\right)}{1\,000 \times V} \quad (2)$$

where

$\rho_{As,0}$ is the mean concentration of arsenic, in micrograms per millilitre, in the blank test solutions;

$\rho_{As,1}$ is the concentration of arsenic, in micrograms per millilitre, in the sample solution;

V is the volume, in cubic metres, of the air sample;

V_0 is the volume, in litres, of the blank test solution; i.e. 0,02 l;

V_1 is the volume, in litres, of the sample solution; i.e. 0,02 l;

F_0 is the dilution factor used in the preparation of the blank test solution;

F_1 is the dilution factor used in the preparation of the sample solution;

1 000 is the factor used to convert the result to milligrams per cubic metre.

11.2 Method performance

Laboratory experiments indicate that the analytical method does not exhibit significant bias, except the lowest analysed concentration of this method, which resulted in a slightly higher relative standard deviation.

The mean precision and analytical recovery for dosed filters in the range of 0,2 µg to 2 µg of arsenic was determined to be > 95 % with a relative standard deviation < 2,5 %, except the relative standard deviation for dosed filters of 0,2 µg, which amounted to 11 %. The recovery on cellulose nitrate filters for arsenic and arsenic compounds was stable over four weeks studied.

The target values for quantification limits depend on the applicable local limit value. According to ISO 20581, limits of quantification should be 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.

For this method the instrumental detection limit, the detection limit and quantification limit meet the requirements specified in ISO 21832.

The expanded uncertainty of the method has been determined on three concentrations for arsenic including the uncertainty of sampling and analysis according to the requirements of ISO 21832 (see 10.5). Using a coverage factor of 2, an expanded uncertainty between 15 % and 33 % can be determined for arsenic.

11.3 Remarks

The selectivity of the method depends mainly on the choice of wavelength and the presence of spectral interference. For non-spectral interferences such as more complex matrix effects, it is recommended to use the standard addition method. The best results are achieved at a wavelength of 193,7 nm. The resonance wavelengths at 189,0 nm and 197,3 nm are less sensitive. Electrodeless discharge lamps (EDL) should be used as the source of radiation, as they have a much higher radiation flux density than hollow cathode lamps (HCL). Measurements with EDL are much more sensitive and also deliver a better signal/noise ratio.

The load on the graphite tube or the graphite platform in the atomic absorption spectrometry is strongly dependent on the matrix of the samples to be analysed. For the specified temperature/time programme, the stability of the graphite furnace and thus the constancy of the recovery for samples with low arsenic content is about 24 h.

With unknown sample compositions, longer heating steps at higher temperatures are necessary, which have a strong influence on the lifetime of the graphite components. If the presence of graphite-modifying substances (e.g. carbide formers such as tungsten, vanadium or tantalum) cannot be excluded, recalibrations shall be carried out after each sample.

12 Test report

12.1 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) all details necessary for 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 6323-1:2024);

d) the brand, type and diameter of filter used;

e) the brand and type of sampler used;

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

g) the brand 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 during the sampling period, in litres per minute;

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

k) the volume, 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 arsenic and arsenic compounds 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 arsenic in the sample and blank solutions, the volumes of the sample and blank solutions, and the dilution factor; any interferents known to be present shall be recorded;

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 arsenic 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[6] 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; and

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

12.2 Laboratory report

The laboratory report shall contain all information required by the end user.