

Arsenic – Determination of arsenic and its particulate compounds in workplace air using atomic absorption spectrometry (GF-AAS)

Air Monitoring Method

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Abstract

This analytical method is a validated measurement procedure for the determination of arsenic [7440-38-2] and its particulate compounds e.g. arsenic trioxide [1327-53-3] and arsenic triiodide [7784-45-4] after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a nitrocellulose membrane filter using a suitable flow-regulated pump. After acid digestion, the arsenic retained on the filter is analysed using graphite furnace atomic absorption spectrometry (GF-AAS). The relative limit of quantification (LOQ) is 0.11 µg As/m³ for an air sample volume of 1.2 m³. The mean recovery for arsenic was 100%. The concentration-dependent expanded uncertainty was 15% to 33%. This analytical method has been accredited by the accident insurance companies for the detection in workplace air of substances that are carcinogenic, mutagenic or toxic to reproduction. This method has been tested and recommended for the determination of arsenic in work areas by the German Social

Accident Insurance (DGUV). Both personal and stationary sampling can be performed for measurements in order to evaluate work areas.

Name	CAS No.	Molar mass [g/mol]	Formula	Substance-specific concentration values [$\mu\text{g As}/\text{m}^3$]
Arsenic	7440-38-2	74.92	As	-
Arsenic compounds, classified as C1A, C1B				TC 8.3 (I) EF 8 (AGS 2021, 2023) AC 0.83 (I) (AGS 2021, 2023)
Arsenic trioxide	1327-53-3	197.84	As ₂ O ₃	See above
Arsenic triiodide	7784-45-4	455.65	AsI ₃	See above

AC: acceptable concentration; TC: tolerable concentration; I: inhalable fraction; EF: excursion factor

1 Summary

The mean concentration of arsenic and its particulate compounds at the workplace over the sampling period can be determined with this method using personal or stationary sampling.

Measurement principle: A pump is used to draw a defined volume of air through a membrane filter. The fraction deposited on the filter is analysed for arsenic using an atomic absorption spectrometer with graphite furnace technique after acid digestion.

Limit of quantification (calculated as As):
 Absolute: 0.13 μg of arsenic per sample carrier
 Relative: 0.11 $\mu\text{g}/\text{m}^3$ for an air sample volume of 1.2 m^3 (a sampling period of 2 h at 10 l/min, a dilution factor of 4, an injection volume of 20 μl and 5 μl matrix modifier)

Measurement range: 0.11 to 1.7 $\mu\text{g}/\text{m}^3$ based on an air sample volume of 1.2 m^3 .

Selectivity: The selectivity of the method depends above all on the selection of the wavelength, the absence of spectral interference and the minimisation of non-spectral interference. Carbide-forming sample components can lead to diminished values.

Advantages: Personal measurements with high sensitivity are possible; suitable for short-term measurements.

Disadvantages: No indication of concentration peaks, requires costly resources in terms of technology and time.

Apparatus:
 Sampling devices:
 Pump and sampling head, filter holder with membrane filter and supporting sieve
 Volumetric flow meter
 Digestion system
 Atomic absorption spectrometer with graphite furnace (graphite furnace with L'vov platform, pyro-coated) and Zeeman background correction

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Pump suitable for personal or stationary sampling with a nominal volumetric flow rate of 10 l/min (e.g. SG10-2, from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- GSP 10 sampling head (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- PGP filter cassette made of plastic supplied with covers for filters of 37 mm diameter (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Supporting sieve, 37 mm (e.g. from Metaq GmbH, 42115 Wuppertal, Germany)
- Membrane filter, diameter 37 mm, pore width 8.0 µm, nitrocellulose, if possible with a test certificate stating the content of metals (e.g. from Sartorius AG, 37075 Göttingen, Germany)
- Volumetric flow meter (e.g. from TSI GmbH, 52068 Aachen, Germany)

For the sample preparation:

- Heating block thermostat made of metal or graphite with time/temperature control, operating range up to 200 °C (e.g. from Gebr. Liebisch GmbH & Co. KG, 33649 Bielefeld, Germany)
- Graduated digestion vessels with air cooler made of quartz glass (diameter 19 mm, maximum volume 25 ml) with ground joints (NS 19/26), acid-proof 0.2 ml graduation in the range from 15 to 25 ml (e.g. from VWR International GmbH, 64295 Darmstadt, Germany)
- Graduated digestion vessels with air cooler made of quartz glass (28 mm diameter, maximum volume of 100 ml) with ground joints (NS 29/32), acid-proof 0.5 ml graduation in the range from 75 to 100 ml (e.g. from VWR International GmbH, 64295 Darmstadt, Germany)
- Glass rods (diameter approx. 4 mm), made of quartz glass (usual glass rods cannot be cleaned residue-free) with attached replaceable end pieces made of PTFE tube (e.g. from VWR International GmbH, 64295 Darmstadt, Germany)
- Stoppers made of polyethylene for the digestion vessels (NS 19/26 and NS 29/32) (e.g. from Pöppelmann GmbH & Co. KG, 49378 Lohne, Germany)
- 5-l bottle made of perfluoroalkoxy copolymer (PFA) with PTFE dispenser for rinsing the air cooler or preparing dilutions (e.g. Fortuna Optifix HF Dispenser, 30 ml, from Poulten & Graf GmbH, 97877 Wertheim, Germany)
- Measuring cylinders made of PFA, 500 ml, 100 ml, 50 ml (e.g. from VITLAB GmbH, 63762 Großostheim, Germany)
- 2.5-litre quartz bottle with lateral filler neck (NS 29/32), sealable with air-permeable PTFE ground stopper and PTFE (“hydrofluoric acid”) dispenser as a bottle attachment, custom-made device (e.g. from Merck Eurolab GmbH, 53797 Lohmar, Germany); purpose of application: to dispense of recently prepared acid mixtures into the digestion vessels
- Ceramic tweezers to transfer the membrane filters into the digestion vessels (e.g. from PLANO GmbH, 35578 Wetzlar, Germany)

For analytical determination:

- Atomic absorption spectrometer with graphite furnace technique, preferably with Zeeman background correction and autosampler; graphite furnace with L’vov platform, pyro-coated and arsenic hollow cathode lamp
- Volumetric flasks made of PFA for standard and calibration solutions with screw caps and ring marks, 1000 ml, 500 ml, 100 ml, 50 ml, 10 ml, 5 ml (e.g. from VITLAB GmbH, 63762 Großostheim, Germany)

- Disposable polystyrene vessels, volume approx. 1.5 ml for the autosampler (e.g. from Greiner Bio-One, 72636 Frickenhausen, Germany)
- Various adjustable piston pipettes to cover a volume range of 2 µl to 10 ml, air displacement: for aqueous solutions and suspensions at a density and viscosity similar to water (e.g. Socorex Acura 825® (2 to 1000 µl), Socorex Acura 835 (500 to 5000 µl) & Socorex Acura 835 (1000 to 10000 µl), from Socorex Isba S.A., Ecublens, Switzerland)
- Electronic precision balance
- Ultrapure water unit with reverse osmosis device and ultrapure water system, for the preparation of ultrapure water (specific resistance $\geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 °C), reduction of the general metal content, in particular for the production of water that is low in boron and alkaline metals (e.g. GenPure with X-CAD, from Wilhelm Werner GmbH, 51381 Leverkusen, Germany)

2.2 Chemicals

- Ultrapure water (specific resistance $\geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 °C)
- Nitric acid, 65%, low metal content, contents certified by the manufacturer for each batch (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Hydrochloric acid, 30%, low metal content, contents certified by the manufacturer for each batch (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Nitric acid, 67 to 70%, low metal content, contents certified by the manufacturer for each batch (e.g. nitric acid, INSTRA-ANALYZED Plus for the trace analysis of metals, J.T. Baker, from VWR International GmbH, 64295 Darmstadt, Germany)
- Nickel plasma standard solution, 1000 mg/l, Specpure, traceable to SRM from NIST, $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in HNO_3 , 5% (e.g. Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76185 Karlsruhe, Germany, Order No. 13839)
- Arsenic single element ICP standard, 1000 mg/l, Certipur, traceable to SRM from NIST, H_3AsO_4 in HNO_3 , 2 to 3% (e.g. from Merck KGaA, 64293 Darmstadt, Germany, Order No. 170300100)
- Multi-element quality control standard, 100 mg/l for 33 elements, ARISTAR for ICP, traceable to SRM from NIST (e.g. from VWR International GmbH, 64295 Darmstadt, Germany, Order No. 84791.180)
- D129-3, CrAlNiMo-alloy nitrided steel 34CrAlNi7, steel grade No. 1.8550, Euronorm-CRM, Bundesanstalt für Materialforschung und -prüfung (BAM), 12489 Berlin, Germany
- D187-1, low-alloyed boron steel, Euronorm-CRM, Bundesanstalt für Materialforschung und -prüfung (BAM), 12489 Berlin, Germany
- Arsenic(III) oxide, 99.996% (metal basis excluding Sb), 20 ppm max. of Sb, powder (e.g. PURATRONIC, Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76185 Karlsruhe, Germany, Order No. 11173)
- Arsenic(III) iodide, 99.999% (metal basis), 80 mesh powder (e.g. Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76185 Karlsruhe, Germany, Order No. 41962)
- Argon 5.0 (purity at least 99.999%).

2.3 Solutions

The following solutions were prepared using the chemicals listed in [Section 2.2](#):

Acidic digestion mixture: solution of 2 parts of nitric acid (65%) and 1 part of hydrochloric acid (25%) (v/v)
1400 ml of 65% nitric acid are mixed in a 2.5-l quartz bottle with a solution of 130 ml of ultrapure water and 570 ml of 30% hydrochloric acid.

Modifier solution: solution of 1000 mg Ni/l

The matrix modifier improves the separation of matrix and analyte during the pyrolysis step. Additionally, the pyrolysis temperature can be increased without evaporation of the analyte.

Blank value solution:

50 µl of 70% nitric acid are added to a 5-ml volumetric flask into which approx. 4.5 ml of ultrapure water have been previously placed. The flask is then filled to 5 ml with ultrapure water and shaken.

AAS rinsing solution:

5 ml of 65% nitric acid are added to a 1000-ml volumetric flask into which approx. 900 ml of ultrapure water have been previously placed. The flask is then filled to 1000 ml with ultrapure water and shaken.

Acid mixture: for the preparation of the calibration, quality control and sample solutions

5 ml of 70% nitric acid are added to a 500-ml volumetric flask into which approx. 400 ml of ultrapure water have been previously placed. The flask is then filled to 500 ml with ultrapure water and shaken.

As stock solution 1: solution of 10 mg As/l

1 ml of arsenic ICP standard (c = 1000 mg/l) is pipetted into a 100-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

As calibration solution 1: solution of 8 µg As/l

80 µl of arsenic stock solution 1 (c = 10 mg/l) are pipetted into a 100-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

As calibration solution 2: solution of 25 µg As/l

250 µl of arsenic stock solution 1 (c = 10 mg/l) are pipetted into a 100-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

Control stock solution: solution of 1000 µg As/l

1 ml of the multi-element quality control standard (100 mg/l) is pipetted into a 100-ml volumetric flask, which is then filled to the mark with the above-mentioned acid mixture and shaken.

Control solution 1: solution of 5 µg As/l

500 µl of the control stock solution (c = 1000 µg/l) are pipetted into a 100-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

Control solution 2: solution of 20 µg As/l

2 ml of the control stock solution (c = 1000 µg/l) are pipetted into a 100-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

As spiking stock solution 1: solution of 20 mg As/l

1 ml of the arsenic single element ICP standard (1000 mg/l) is pipetted into a 50-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

As spiking stock solution 2: solution of 40 mg As/l

2 ml of the arsenic single element ICP standard (1000 mg/l) are pipetted into a 50-ml volumetric flask, which is then filled to the mark with the acid mixture and shaken.

As spiking stock solution 3: solution of 4000 µg As/l

The solution of 4000 µg As/l is prepared by means of an intermediate dilution (100 mg/l). For this purpose, 5 ml of the arsenic single element ICP standard (1000 mg/l) are pipetted into a 50-ml volumetric flask. The flask is then filled to the mark with the acid mixture and shaken. 2 ml of the intermediate dilution with a concentration of 100 mg/l of arsenic are pipetted into a 50-ml volumetric flask. The flask is then filled to the mark with the acid mixture and shaken.

The acid-stabilised solutions are stable over a storage period of at least four weeks in the concentration range presented here.

Control samples must be freshly prepared each working day.

3 Sampling

Before measurements are carried out, the filter batch used must be checked for its content of metals and therefore its suitability in complying with the minimum requirements for performance of the measurement procedures.

The filter capsule is equipped with the membrane filter (Ø 37 mm) and the supporting sieve, inserted into the GSP 10 sampling head, which is then connected to the pump. A volumetric flow rate of 10 l/min is set. The definition of the inhalable dust is fulfilled at this volumetric flow rate (DIN 1993). At a sampling period of two hours, this corresponds to an air sample volume of 1.2 m³.

Sampling can be carried out as stationary or personal sampling. Measurements are taken in the breathing zone in the case of personal sampling. It is important to ensure that the inlet of the sampling head is freely accessible.

After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted volumetric flow rate is greater than ± 5%, it is advisable to repeat the measurement (see DGUV Information 213-500 “General Part”, Section 3 in DGUV 2015).

The loaded membrane filter is then removed from the sampling system, sealed with the filter capsule caps and transported to the laboratory for analysis with as little vibration as possible.

It is recommended that the membrane filters are used exclusively for the determination of metals in order to eliminate losses in other processing steps, e.g. weighing.

4 Analytical determination

4.1 Sample preparation

Ceramic tweezers are used to fold the loaded membrane filter carefully and to transfer it into a 25 ml digestion vessel. A glass rod is used to push it down to the bottom of the vessel. Then, 10 ml of the acid digestion mixture are added to the filter. The vessel, fitted with an air cooler, is heated in a thermostat with aluminium heating block for two hours under reflux (block temperature approx. 135°C). After cooling to a temperature of approx. 50°C, 10 ml of ultrapure water are carefully added through the air cooler to rinse it and simultaneously dilute the solution, which may be slightly viscous in some cases. The solution is again heated to boiling point. After cooling, the air cooler and the glass rod are removed, the digestion vessel is sealed with a polyethylene stopper and the volume of the sample solution is read off. The sample solution is then diluted with the acid mixture (see Section 2.3), immediately before analytical determination in the analytical device (measurement solution) (Pitzke et al. 2018, 2019).

A current blank value is determined with each series of samples. For this purpose, at least two unused filters from the same batch are subjected to the entire sample preparation and analysed. This current blank value may only differ at most by three times the standard deviation from the mean blank value determined as part of the development of the method. If this is not the case, a mean blank value must be determined anew as stipulated in Section 6.3.

4.2 Operating conditions

The characteristics of the method described in Section 6 were determined under the following operating conditions:

Apparatus:	Atomic absorption spectrometer with graphite furnace (GF-AAS) “AAS ZEE nit 650 BU” from Analytik Jena, “MPE 60 graphite autosampler”, integrated circulation cooler Graphite furnace with L’vov platform, arsenic hollow cathode lamp, warm-up period at least 15 minutes
Absorption	193.7 nm
Slit width:	0.8 nm
Lamp current:	7 mA
Background compensation:	Zeeman mode two field
Measurement solution:	An aliquot of the sample solution (see Section 4.1) is diluted with three parts of the acid mixture ^{a)} (see Section 2.3)
Injection volumes:	20 µl of the measurement solution and 5 µl of the matrix modifier; injection is performed by the autosampler

^{a)} As a rule, a dilution of 1:4 is sufficient for a measurement free of interference. If the matrix of the measurement solution is too concentrated or the arsenic content is too high, then it must be further diluted.

Tab. 1 Temperature/time program

Program step	Explanation	Heating rate [°C/s]	Oven temperature [°C]	Dwell time [s]	Argon rinsing gas
1	Injection/drying	5	85	20	max.
2	Drying	3	95	15	max.
3	Drying	2	105	10	max.
4	Pyrolysis	50	350	20	max.
5	Pyrolysis	250	1000	10	max.
6	Auto zero	0	1000	5	stop
7	Atomisation/measurement	max.	2450	4	stop
8	Heating	max.	2600	5	max.

The prepared samples, the blank value solutions and filter blank value solutions are analysed by AAS. For this purpose, the samples and filter blank value solutions are diluted in advance with the acid mixture described in Section 2.3 at a ratio of 1:4. In each case, 20 µl of the solution to be investigated are injected into the graphite furnace with 5 µl of the modifier solution using the autosampler and analysed according to the AAS operating conditions listed above. Each sample is analysed in duplicate and the mean value is used for calculating the result. Rinsing of the AAS system is carried out with the rinsing solution specified in Section 2.3.

If arsenic concentrations above the calibration range are detected, the sample solutions are further diluted and analysed anew as described above.

Following calibration, after a maximum of 20 to 25 sample measurements and at the end of the sequence, the control solutions are analysed. These must fall within defined limits (e.g. ±10%), otherwise the calibration must be checked and the analysis of the sample solution must be repeated. Thus, the stability of the analytical devices and the accuracy of the results are checked.

An electronic blank value adjustment is carried out after each measurement. The blank value is analysed regularly, at the latest every 20th to 25th sample, by measuring the blank value solution and the signal (area) is adjusted to zero. Subsequently, a complete recalibration is always performed.

5 Evaluation

5.1 Calibration

The calibration must be performed every working day. In order to obtain the calibration function, arsenic calibration solutions 1 (8 µg/l) and 2 (25 µg/l) (see Section 2.2) are prepared from arsenic stock solution 1 ($c = 10$ mg/l, see Section 2.2). Calibration samples are prepared using the autosampler with a constant injection volume of 25 µl in total and measured (see Table 2). Dilution of the calibration solution with the acid mixture is performed automatically (see Section 2.3). Additionally, 5 µl of the modifier solution are also added by means of the autosampler. The calibration samples are analysed under the AAS operating conditions as described in Section 4.2.

Tab. 2 Dilutions to obtain the calibration function

Calibration sample	Arsenic concentration in the calibration solution [µg/l]	Volume of the calibration solution [µl]	Volume of the acid mixture [µl]	Volume of the matrix modifier [µl]	Concentration of As ^{a)} [µg/l]
0	0	0	20	5	0
1	8	6	14	5	2.4
2	8	12	8	5	4.8
3	8	20	0	5	8.0
4	25	10	10	5	12.5
5	25	15	5	5	18.8
6	25	20	0	5	25.0

^{a)} The volume of the matrix modifier is not taken into account for the calculation of the concentration as it is also added to the analytical samples.

The absorptions are determined from the peak areas, which are plotted versus the concentrations. The graph of the calibration function is linear under the stated conditions.

5.2 Calculation of the analytical result

The concentration of arsenic in the workplace air is calculated from the concentration of arsenic in the measured solution calculated by the software from the measured absorption. The calculated calibration function is used by the software for this purpose. The concentration of arsenic in the workplace air is calculated from the measured arsenic concentrations, taking the corresponding dilutions and the air sample volume into account.

The mass concentration of arsenic in the air sample in µg/m³ is calculated according to Equation 1 as follows:

$$\rho = \frac{((c \times fv_c) - (c_{Blank} \times fv_{cBlank})) \times V_{SOL}}{V \times \eta} \quad (1)$$

where:

- ρ is the mass concentration of arsenic in the air sample in µg/m³
- c is the concentration of arsenic in the measured solution in µg/l
- fv_c is the dilution factor of the sample (as a rule the dilution is 1:4)
- c_{Blank} is the concentration of the blank value (mean value) in µg/l in the measured solution
- fv_{cBlank} is the dilution factor of the blank value (as a rule the dilution is 1:4)
- V_{SOL} is the volume of the prepared sample solution in l

- V is the air sample volume in m^3
 η is the recovery (= 1, see Section 6.2)

6 Reliability of the method

The characteristics of the method were calculated as stipulated in DIN EN ISO 21832 (DIN 2020), DIN EN 482 (DIN 2015) and DIN 32645 (DIN 2008).

6.1 Precision

In order to determine the precision, six membrane filters were each loaded with different masses of arsenic (0.2 μg , 1.0 μg and 2.0 μg). The samples were subsequently digested as described in Section 4.1, then prepared and analysed (Section 4.2).

For this purpose, arsenic spiking stock solution 1 with a concentration of 20 mg/l was prepared from the arsenic standard solution of 1000 mg/l by means of an intermediate dilution (see Section 2.3). Six filters were each spiked with 10 μl of this spiking stock solution 1 (this is equivalent to an arsenic content of 0.2 μg per filter).

A further six filters were each spiked with 50 μl and another six filters were each spiked with 100 μl of spiking stock solution 1 (this is equivalent to an arsenic content of 1.0 μg and 2.0 μg). The filters were dried at room temperature for 24 hours. The filters spiked in this way were prepared and analysed in the same manner as the sample solutions.

For an air sample volume of 1200 l, these spiked masses are equivalent to concentrations of arsenic in air of 0.17 $\mu\text{g}/\text{m}^3$, 0.83 $\mu\text{g}/\text{m}^3$ and 1.7 $\mu\text{g}/\text{m}^3$.

The digestion solutions with spiked masses of 10 μl , 50 μl and 100 μl were diluted with the acid mixture by a factor of 4 before analysis by means of the GF-AAS. Furthermore, two unused filters were subjected to the complete analytical method.

The precision data shown in Table 3 were calculated from these results.

Tab. 3 Precision data

Spiked mass of arsenic [μg]	Concentration of arsenic ^{a)} [$\mu\text{g}/\text{m}^3$]	Relative standard deviation [%]
0.20	0.17	11
1.0	0.83	2.4
2.0	1.7	1.9

^{a)} The concentration is calculated on the basis of a 2-hour sampling period at a volumetric flow rate of 10 l/min.

6.2 Recovery

As a result of the different chemical composition and the different physical properties of the aerosols in different work areas, it is impossible to provide generally valid data on the recovery rate for the entire procedure.

The analytical recovery is defined as 100% on the basis of the sample preparation described above according to DIN EN ISO 21832 (DIN 2020) (valid only for those metals and compounds that are soluble in the stated system).

Certified arsenic and arsenic compounds (see Section 2.2) were used for checking the described sample preparation method with regard to the analytical recovery and the reproducibility of the method.

Recovery experiments were performed with arsenic trioxide and arsenic triiodide (see Section 2.2).

As the arsenic concentrations to be examined are in the ultratrace range and therefore reliable weighing of reference materials is difficult, the following procedure was selected:

Approx. 10 mg of arsenic trioxide or arsenic triiodide were weighed onto two nitrocellulose filters in each case. Each filter was then transferred into a 100-ml digestion vessel with four unused nitrocellulose filters. After addition of 50 ml of the digestion solution, they were boiled over a period of two hours under reflux (see Section 2.1, 2.2, 2.3 and 4.1). After digestion, 50 ml of ultrapure water were added through the air cooler and the solution was again heated to boiling point. The solutions prepared in this manner were visually free of particles. A reading of the volume was taken after digestion.

The reference material solutions prepared as described above contained an arsenic concentration of 37 870 µg/l for arsenic trioxide and of 16 443 µg/l for arsenic triiodide. These reference material solutions were diluted so that they corresponded to arsenic concentrations of 0.17 µg/m³, 0.83 µg/m³ and 1.7 µg/m³ for analysis.

Furthermore, at least two unused filters (blank filters) were subjected to the complete analytical procedure. No blank value correction was carried out to calculate the results.

Quantitative analysis resulted in a mean recovery for arsenic from arsenic trioxide of 0.89 and for arsenic from arsenic triiodide of 1.02.

Further recovery experiments were carried out with reference materials BAM D129-3 and BAM D187-1. BAM D129-3 contained 0.0049% of arsenic, BAM D187-1 contained 0.018% of arsenic. Two amounts of approx. 100 mg were weighed onto one nitrocellulose filter in a 100-ml digestion vessel. Three additional nitrocellulose filters and 40 ml of the digestion solution were added per vessel. The mixtures were boiled for two hours under reflux in (see Section 2.1, 2.2, 2.3 and 4.1). After digestion, 40 ml of ultrapure water were added through the air cooler and the solution was again heated to boiling point. The solutions prepared in this manner were visually free of particles.

The prepared reference material solutions contained a calculated arsenic concentration of 61 µg/l for BAM D129-3 and 225 µg/l for BAM D187-1.

The digestion solutions of the BAM D129-3 and BAM D187-1 reference materials were diluted to corresponding arsenic concentrations of 0.17 µg/m³, 0.83 µg/m³ and 1.7 µg/m³ and analysed.

The recoveries for all reference materials mentioned above are presented as mean values per concentration in Table 4.

Tab. 4 Recoveries of arsenic for 7 determinations

Mass of arsenic on the filter [µg]	Concentration of arsenic [µg/m ³]	Mean recovery [%]	Recovery range [%]	Mean relative standard deviation [%]
0.20	0.17	99.6	69 to 121	23
1.0	0.83	99.6	93 to 106	6.9
2.0	1.7	95.9	85 to 106	10

Arsenic trioxide and arsenic triiodide were present in powder form. For a spiked mass of 0.2 µg of arsenic the recovery for arsenic trioxide was only approx. 70%, whereas for arsenic triiodide it was approx. 94%. The recoveries for the other investigated arsenic concentrations of arsenic trioxide and arsenic triiodide were between 93% and 106%.

The BAM reference materials consisted of fine steel shavings. At a spiked mass of arsenic of 0.2 µg on the filters, recoveries of 112% for D187-1 and 121% for D129-3 were determined for these reference materials. For the arsenic content of 1.0 µg per filter, the recoveries were between 99% and 103%. For arsenic contents of 2.0 µg per filter, a recovery of 95% for the reference material D187-1 was determined and 85% for D129-3.

The tendency for a divergent recovery of the different arsenic contents between the reference materials occurring in powder form and as fine steel shavings is discernible. Due to the possibly heterogeneous sample generation and the standard deviation present in the BAM reference materials, the deviation at these lower contents is higher.

6.3 Limit of quantification

During development of the method, the limit of quantification was determined based on the blank value method defined in DIN 32645 (DIN 2008). For this purpose, ten unused membrane filters were subjected to the entire analytical procedure and the measured values were used for the determination of the limit of quantification.

The absolute limit of quantification according to the blank value method in DIN 32645 (DIN 2008) is 1.6 µg As/l for a confidence interval of 99% and a relative uncertainty of 33%, or $k = 3$. A relative limit of quantification of 0.11 µg As/m³ or of 0.13 µg As per sample carrier is obtained for a digestion volume of 20 ml, a dilution factor of the digestion solution of 4 and an air sample volume of 1.2 m³.

6.4 Storage stability

The storage stability of loaded membrane filters was checked by spiking the filters with 0.2 µg and 2.0 µg of arsenic. For this purpose, the arsenic spiking stock solutions 2 and 3 described in Section 2.3 were used.

Spiking with 2.0 µg of As was performed with 50 µl of arsenic spiking stock solution 2 in each case. This is equivalent to an arsenic concentration of 1.7 µg/m³ for the sampling and analytical conditions described in this method.

50 µl of arsenic spiking stock solution 3 were used for spiking with 0.2 µg of As, which is equivalent to an arsenic concentration of 0.17 µg/m³.

Over a period of four weeks, three filters each on two measurement days were subjected to the entire preparation and analysis procedure. It was shown that the recoveries for both arsenic concentrations were stable over the investigated period.

6.5 Selectivity

The selectivity of the method depends above all on the selection of the wavelength and on the absence of spectral interference. In the case of non-spectral interference, such as complex matrix effects, it is advisable to use the standard addition procedure. The best results are obtained at a wavelength of 193.7 nm. The resonance lines at 189.0 nm and 197.3 nm are less sensitive.

Electrodeless discharge lamps (EDL) should be used as a radiation source, as these have a considerably higher radiation flux density than hollow cathode lamps (HCL). Measurements with EDL are significantly more sensitive than those with HCL and, furthermore, result in a better signal-to-noise ratio (Doerffel and Eckschlager 1981).

6.6 Uncertainty

The expanded uncertainty was obtained by estimation of all the relevant influencing parameters. The uncertainty of the result consists principally of the uncertainty components for sampling and for analysis.

The “QMSys GUM Professional“ software (Qualisyst n.d.) was used to determine the expanded uncertainty. The software is based on Eurachem/CITAC guidance (Ellison and Williams 2012; VDE 2008) according to the requirements of DIN EN ISO/IEC 17025 (DIN 2018). The concentration-dependent expanded uncertainty is calculated taking the uncertainties associated with the air sample volume and the sampling effectiveness for inhalable particles as well as the entire analytical preparation, including digestion, dilution, calibration, equipment drift, recovery and precision into account. The expanded uncertainty for the BAM D129-3 reference material mentioned in Section 2.2 was calculated here as an example.

The combination of all uncertainty contributions results in the concentration-dependent combined uncertainties of the entire method. The values for the expanded uncertainty of the entire method listed in Table 5 are obtained by multiplying with the expansion factor $k = 2$.

Tab. 5 Expanded uncertainty for 6 determinations

Mass of arsenic [μg]	Concentration of arsenic ^{a)} [$\mu\text{g}/\text{m}^3$]	Expanded uncertainty U [%]
0.20	0.17	32.7
1.0	0.83	16.6
2.0	1.7	14.8

^{a)} The concentration is calculated on the basis of a 2-hour sampling period at a volumetric flow rate of 10 l/min.

6.7 Remarks

In the lower measurement range of this method (at approx. $0.17 \mu\text{g}/\text{m}^3$), the determined values had a relative standard deviation of $\geq 5\%$. The measured concentrations are in the range of the lowest calibration point of the calibration function. The measured absorption is relatively low and, in this case, differs only by a factor of approx. 5 from the blank value. Thus, for measurements of arsenic concentrations in the range of $0.17 \mu\text{g}/\text{m}^3$ the relative standard deviation can be greater than 10%. This was observed during analysis of standard solutions as well as in the reference material. The scatter of the values in this lower concentration range is not in accordance with the requirements stipulated in DIN EN ISO 21832 (DIN 2020), however, it is inherent to the method described here and its operating conditions. The precision increases for concentrations of arsenic above the first calibration point.

The wear on the graphite furnace or the graphite platform in the GF-AAS depends largely on the matrix of the sample to be analysed. The stability of the graphite furnace and, therefore, the constancy of the recovery for samples with a low arsenic content lasts approx. 24 hours for the stated temperature/time program.

Longer heating steps at higher temperatures are necessary for unknown sample compositions, which has a strong influence on the lifespan of the graphite parts. If the presence of graphite-altering substances (e.g. carbide-forming substances such as tungsten, vanadium or tantalum) cannot be ruled out, recalibration must be carried out after each sample.

6.8 Comparison of open digestion with high-pressure microwave technology

In the context of a comparative experiment, the open digestion described here was compared with the high-pressure microwave-assisted digestion, which is stated as an alternative digestion procedure (Pitzke et al. 2018, 2019). For this purpose, filters spiked with arsenic ($0.2 \mu\text{g}$ of arsenic, see Section 2.2) were prepared and analysed. The determined recoveries for arsenic were 101% for the high-pressure microwave-assisted digestion and 95% for the open digestion with the analytical method described here. Thus, the achievable recoveries with both digestion methods are similar.

Notes

Competing interests

The established rules and measures of the Commission to avoid conflicts of interest (www.dfg.de/mak/conflicts_interest) ensure that the content and conclusions of the publication are strictly science-based.

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