

Germanium – Determination of germanium and its non-volatile inorganic compounds in workplace air using inductively coupled plasma mass spectrometry (ICP-MS)

Air Monitoring Method – Translation of the German version from 2023

Keywords

germanium; air analyses; analytical method; workplace measurement; hazardous substance; inductively coupled plasma mass spectrometry; inhalable particles; ICP-MS; membrane filter; microwave-assisted pressure digestion

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Abstract

The working group “Air Analyses” of the German Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) developed and verified the presented analytical method. This analytical method is a validated measurement procedure for the determination of germanium [7440-56-4] and its non-volatile compounds in workplace air in a concentration range of one tenth up to twice of the currently valid Occupational Exposure Limit Value (OELV) in Germany of 0.85 mg/m³ as germanium in the inhalable particle fraction. For sampling, a defined volume of air is drawn through a membrane filter (nitrocellulose). The flow rate is 10 l/min and sampling duration is 2 hours. Germanium is digested with a mixture of hydrofluoric and nitric acid in a microwave-assisted pressure digestion. The samples are subsequently analysed using mass spectrometry with inductively coupled plasma (ICP-MS). The quantitative determination is based on a calibration function. The limit of quantification is 0.004 µg/m³ for an air sample volume of 1200 l and 20 ml digestion volume. The mean recovery is 97.2% for germanium and 97.9% for germanium dioxide. The expanded uncertainty for the validation range of 0.085 to 1.7 mg/m³ is 35.7 to 24.4%.

Method number	1
Application	Air analysis
Analytical principle	Inductively coupled plasma mass spectrometry (ICP-MS)

1 Characteristics of the method

Precision:	Standard deviation (rel.):	$s = 1.6\text{--}5.0\%$
	Expanded uncertainty:	$U = 24.4\text{--}35.7\%$
	in the concentration range from 0.004 to 1.7 $\mu\text{g}/\text{m}^3$ and for $n = 8$ determinations	
Limit of quantification:	0.004 $\mu\text{g}/\text{m}^3$ for an air sample volume of 1200 l and a sampling period of 2 h	
Recovery:	$\eta = 94.7\text{--}99.3\%$	
Sampling recommendations:	Sampling period:	2 h
	Air sample volume:	1200 l
	Volumetric flow rate:	10 l/min
	For short-term measurements:	15 min; 10 l/min

2 Description of the substance

Germanium [7440-56-4]

Germanium is a light grey, brittle and, in the form of a fine powder, a flammable main group metal that is represented by the symbol Ge (relative atomic mass: 72.59 u, melting point: 947.4 °C, boiling point: 2830 °C, density: 5.323 g/cm³).

Germanium is a metalloid belonging to group IV, period 4 of the periodic table. It is chiefly produced as a by-product of zinc or lead-zinc-copper ore processing (Swennen et al. 2000). It is a semiconductor. Elemental germanium is mainly used in infrared optics and in the manufacture of photodetectors. Germanium tetrachloride is used in the manufacture of optical fibres. Germanium dioxide is primarily used as a catalyst in the production of polyester and synthetic textile fibres (Roels and Buchet 2001; Scoyer and Wolf 1997, p. 1505–1524).

Little is known about the toxicity of germanium after inhalation exposure. No data for acute toxicity in humans are available. After repeated exposure to germanium at the workplace, no relationship was found between disorders of the kidneys, liver and respiratory tract and ongoing exposure to germanium. A clinical assessment of lung function likewise revealed no effects (AGS 2018).

Germanium and germanium dioxide have been assigned an OELV of 0.85 mg/m³ (inhalable fraction (I)) and an excursion factor of 2 (AGS 2023). A MAK value (maximum concentration at the workplace) has not been derived (DFG 2023).

3 General principles

This analytical method is used to simultaneously determine the levels of germanium and non-volatile germanium compounds in the workplace air in a concentration range from one tenth up to twice the currently valid OELV of 0.85 mg/m³ I. The method is also suitable for monitoring compliance with the short-term value.

Samples are taken by drawing a defined volume of air through a membrane filter (nitrocellulose) by means of a suitable sampling pump. After acid digestion, the germanium deposited on the filter is detected by inductively coupled plasma mass spectrometry. The quantitative evaluation is based on a calibration function, whereby the quotient obtained from

the concentrations of germanium in the calibration standards and the yttrium internal standard are plotted against the measured intensities.

4 Equipment, chemicals and solutions

4.1 Equipment

For sampling:

- Sampling pump for personal and stationary sampling (maintains adequate performance in spite of the drop in pressure caused by the inserted carriers), suitable for a flow rate of 10 l/min as specified by DIN EN ISO 13137 (DIN 2023) (e. g. SG10-2, from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- GSP 10 sampling head for personal sampling (e. g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- PGP filter cassette made of plastic with covers for the filters with a diameter of 37 mm (e. g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Membrane filter, Ø 37 mm, pore size 8.0 µm, nitrocellulose. Each batch analysed for metal content (e. g. nitrocellulose membrane filter, from Sartorius AG, 37079 Göttingen, Germany (or filters of comparable quality))
- Supporting sieve, 37 mm (e. g. from Metaq GmbH, 42115 Wuppertal, Germany)
- Gas meter or flow meter (e. g. TSI Flowmeter 4146, from TSI GmbH, 52068 Aachen, Germany)

For sample preparation:

- Equipment for carrying out microwave-assisted pressure digestion with temperature and pressure controls (e. g. ultraCLAVE, from MLS Mikrowellen-Labor-Systeme GmbH, 88299 Leutkirch im Allgäu, Germany)
- Sample vials with loose-fitting caps made of polytetrafluoroethylene (PTFE) for microwave-assisted pressure digestion (e. g. from MLS Mikrowellen-Labor-Systeme GmbH, 88299 Leutkirch im Allgäu, Germany)
- 500-ml bottle made of perfluoroalkoxy-copolymer (PFA) with PTFE dispenser
- PTFE racks for the sample vials used in the microwave-assisted pressure digestion system (e. g. for up to 40 samples, from MLS Mikrowellen-Labor-Systeme GmbH, 88299 Leutkirch im Allgäu, Germany)
- Disposable centrifuge tubes made of polypropylene (PP) with screw caps, graduated, nominal volume 15 ml, 50 ml (e. g. from Greiner AG, Kremsmünster, Austria)
- 500-ml vessel made of PFA with PTFE dispenser
- 500-ml spray bottle made of PFA with closure made of PP
- Graduated cylinders made of PFA, maximum nominal volumes 100 and 500 ml
- Ceramic tweezers
- Electronic precision balance, suitable for sample weights in the range of 3 to 10 mg

For the analytical determination:

- Quadrupole ICP mass spectrometer with a collision/reaction cell and autosampler (e. g. ICP-MS NexION 350D, from PerkinElmer LAS GmbH, 63110 Rodgau, Germany)
- Concentric PFA nebuliser (e. g. Apex-ST PFA MicroFlow, flow rate 100–200 µl/min, from PerkinElmer LAS GmbH, 63110 Rodgau, Germany)
- Concentric nebuliser with PFA Scott spray chamber (e. g. from PerkinElmer LAS GmbH, 63110 Rodgau, Germany)
- Vessels to hold standard solutions, calibration standards and samples for ICP-MS

- PP vessels with screw caps (tested for blank values), graduated, 0.5-ml increments, maximum volume 15 ml, for the autosampler
- Vessels, e.g. made of PP, for storing the rinsing solution for the autosampler (5 l)
- Vessels, e.g. made of PFA for storing the dilution solution (2 l) or made of PP for storing the rinsing solution for the autosampler (5 l) or made of PFA for storing the mobile phase for the ICP-MS (500 ml)
- Positive displacement dispenser system for precise and automated sequential dosing of internal standard and for bringing to volume with dilution solution (e.g. Microlab 600, from Hamilton Bonaduz AG, Switzerland)
- Various adjustable piston pipettes to cover a volume range of 10 μ l to 5 ml, air displacement for aqueous solutions and suspensions at a density and viscosity similar to water (e.g. from Socorex Isba S.A., Ecublens, Switzerland)
- Ultrapure water system with reverse osmosis unit for the preparation of ultrapure water ($\rho \geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 $^{\circ}\text{C}$), for the reduction of the overall metal content, in particular for the production of water that is low in boron and alkalis (e.g. Milli-Q, from Merck KGaA, 64293 Darmstadt, Germany)

4.2 Chemicals

- Nitric acid, 65%, low metal content, batch certification by the manufacturer (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Nitric acid, approx. 67–69%, low metal content, batch certification by the manufacturer (e.g. J.T.Baker INSTRA-ANALYZED Plus for the trace analysis of metals, from Fisher Scientific GmbH, 58239 Schwerte, Germany)
- Hydrofluoric acid, 40%, low metal content, batch certification by the manufacturer (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Yttrium standard for ICP, 1000 $\mu\text{g/ml}$, Y_2O_3 in 5% HNO_3 (e.g. Specpure, traceable to NIST SRMs, Alfa Aesar, from Fisher Scientific GmbH, 58239 Schwerte, Germany)
- Lutetium standard for ICP, 1000 $\mu\text{g/ml}$, Lu_2O_3 in 2–3% HNO_3 (e.g. Certipur, traceable to NIST SRMs, from Merck KGaA, 64293, Darmstadt, Germany) *not absolutely necessary, see Note*
- Scandium standard for ICP, 1000 $\mu\text{g/ml}$, Sc_2O_3 in 7% HNO_3 (e.g. Certipur, traceable to NIST SRMs, from Merck KGaA, 64293, Darmstadt, Germany) *not absolutely necessary, see Note*
- Tellur standard solution for ICP, 1000 $\mu\text{g/ml}$, Te in 5% HNO_3 (e.g. Specpure, traceable to NIST SRMs, Alfa Aesar, from Fisher Scientific GmbH, 58239 Schwerte, Germany) *not absolutely necessary, see Note*
- Germanium standard solution for ICP, 1000 $\mu\text{g/ml}$, Ge in 5% $\text{HNO}_3/\text{tr. HF}$ (e.g. Specpure, Alfa Aesar, from Fisher Scientific GmbH, 58239 Schwerte, Germany)
- Germanium standard solution for ICP, 10 000 $\mu\text{g/ml}$, Ge in 5% $\text{HNO}_3/\text{tr. HF}$ (e.g. Specpure, Alfa Aesar, from Fisher Scientific GmbH, 58239 Schwerte, Germany)
- Germanium powder (≤ 100 mesh), 99.999% (e.g. Alfa Aesar, from Fisher Scientific GmbH, 58239 Schwerte, Germany)
- Germanium dioxide powder, > 99% (e.g. from Merck KGaA, 64293 Darmstadt, Germany)
- B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W and Zr multi-element standard (MES 5), 10 $\mu\text{g/ml}$, in H_2O tr. HF/tr. HNO_3 (e.g. TruQ ms Multi-Element Calibration Standard 5, from PerkinElmer LAS GmbH, 63110 Rodgau, Germany, Article No.: N9300235)
- Sb, Hf, Nb, Ta, Sn, W, Ge, Mo, Si, Te, Ti and Zr multi-element standard (71B), 10 $\mu\text{g/ml}$, in 3% $\text{HNO}_3/\text{tr. HF}$ (e.g. IV-ICPMS-71B traceable to NIST SRMs, from Inorganic Ventures, Christiansburg, VA, USA)
- Ultrapure water ($\rho \geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 $^{\circ}\text{C}$)
- Argon 5.0

Note:

Yttrium was chosen for the internal standard for this method. An internal standard that contains several elements (yttrium, lutetium, scandium and tellurium) was used during the development of the method. This internal standard is suitable for routine measurements with different kinds of samples. Lutetium, scandium and tellurium are not required for determining germanium, but do not negatively affect the measurement results for germanium if present.

4.3 Solutions

The following solutions were prepared using the chemicals listed in [Section 4.2](#):

Acid digestion mixture: (65% HNO₃, 40% HF, 10:1 (v/v))

The mixture is not prepared separately before being added to the samples.

A dispenser is used to carefully pipette 9 ml of 65% nitric acid and 0.9 ml of 40% hydrofluoric acid into the PTFE vial that is used for microwave-assisted pressure digestion (see [Section 4.1](#)).

Dilution solution: (0.67–0.69% HNO₃ in water): for the dilution and stabilisation of samples and standards
1.5 l of ultrapure water are placed into a 2-l PFA vessel. 20 ml of 67–69% nitric acid are added and the vessel is filled to 2 l with ultrapure water.

Mobile phase: (0.67–0.69% HNO₃ in water): for the quadrupole ICP mass spectrometer
400 ml of ultrapure water are placed into a 500-ml PFA vessel, 5 ml of 67–69% nitric acid are added and the vessel is filled to 500 ml with ultrapure water.

Rinsing solution: (0.65% HNO₃ in water): for the autosampler/tubes of the quadrupole ICP mass spectrometer
4 l of ultrapure water are placed into a 5-l PP vessel. 50 ml of 65% nitric acid are added and the vessel filled to 5 l with ultrapure water.

Calibration stock solutions: (100 µg/l and 1 µg/l in 0.67–0.69% HNO₃)
100 µl of the multi-element standard (MES 5) are pipetted into a 15-ml centrifuge tube. A dispenser system is used to fill the tube to 10 ml with dilution solution. The stock solution is referred to in the following as “Intermediate dilution 1 MES 5” (ZV 1 MES 5). The elements are present in ZV 1 MES 5 in a concentration of 100 µg/l.

100 µl of this intermediate dilution are transferred by pipette to another centrifuge tube. As described above, the tube is then filled to 10 ml with dilution solution. This stock solution is referred to in the following as “Intermediate dilution 2 MES 5” (ZV 2 MES 5). The elements are present in ZV 2 MES 5 in a concentration of 1 µg/l.

Quality control stock solution: (100 µg/l in 0.67–0.69% HNO₃)
100 µl of the multi-element standard (71B) are pipetted into a 15-ml centrifuge tube. A dispenser is used to fill the tube to 10 ml with dilution solution. The stock solution is referred to as “Intermediate dilution 71B” (ZV 71B). The stock solution has a concentration of 100 µg/l.

Intermediate dilution single-element standard germanium: (1000 mg/l)
1 ml of the single-element standard Ge with an initial concentration of 10 000 µg/ml is pipetted into a 15-ml centrifuge tube before adding 9 ml of dilution solution.

4.4 Calibration and control standards

Internal standard solution: (400 µg Y/l in water)

Internal standards that do not contain an element present in the samples are chosen.

The internal standard solution is prepared by pipetting 0.2 ml of the yttrium standard solution for ICP into a 500-ml volumetric flask made of PTFE. The flask is filled to the mark with dilution solution and shaken. If an internal

standard containing scandium, tellurium and lutetium is also used, then 0.4 ml of the Sc standard (0.8 mg/l), 0.75 ml of the Te standard (1.5 mg/l) and 0.1 ml of the Lu standard (0.2 mg/l) are used to prepare the internal standard solution.

All solutions, including the calibration standards, laboratory blank samples and quality control and sample solutions, are spiked with 0.1 ml of the internal standard solution (to 10 ml). This is equivalent to an yttrium concentration of 4 µg/l.

Calibration standards:

The calibration standards are prepared from calibration stock solutions in concentrations of 100 µg/l (ZV 1 MES 5) and 1 µg/l (ZV 2 MES 5). For this purpose, the stock solutions and the internal standard solution are pipetted into a 15-ml PP vessel in the volumes given in Table 1. A dispenser is then used to fill the vessels to 10 ml with dilution solution. The calibration of germanium and its compounds does not require correction for matrix effects. The range of the analytical procedure is defined as 0.05 to 10 µg/l by the calibration.

Tab. 1 Preparation of the calibration standards

Calibration standard	Volume of ZV 1 MES 5 [µl]	Volume of ZV 2 MES 5 [µl]	Internal standard solution [µl]	Germanium concentration [µg/l]
1	–	500	100	0.05
2	10	–	100	0.1
3	50	–	100	0.5
4	100	–	100	1
5	500	–	100	5
6	1000	–	100	10

Control standards:

Quality control procedures are performed during an analytical run using commercially available solutions (see Section 4.2). The aim is to verify the accuracy of the calibration standard and the stability over the entire measurement period.

The quality control standards are prepared from the quality control stock solution (see Section 4.3) in a concentration of 100 µg/l. For this purpose, the volumes given in Table 2 are pipetted into 15-ml PP vessels, which are then filled to 10 ml with dilution solution using a dispenser (see Section 4.3).

Tab. 2 Preparation of the quality control standards

Concentration of the control standard [µg/l]	Volume of ZV 71B [µl]	Volume of the internal standard solution [µl]
0.1	10	100
1	100	100
10	1000	100

5 Sampling and sample preparation

5.1 Sampling

Samples are collected using stationary or personal sampling procedures. The samples taken by personal sampling are collected within the breathing zone. The inlet of the sampling head must remain unobstructed during sampling.

A membrane filter (nitrocellulose) is inserted into the sampling head (GSP) and a pump is connected. The air is drawn through the membrane filter by means of a flow-regulated pump at a flow rate of 10 l/min. A sampling time of at least two hours is recommended (AGS 2010); if necessary, the sampling time can be extended to up to 8 hours. At a sampling period of two hours, this corresponds to an air sample volume of 1.2 m³. A sampling record of the parameters required for determining the concentrations in air (sample volume, temperature, air pressure and relative humidity) is kept.

The flow rate must be checked for constancy after sampling. If the deviation from the adjusted flow rate is larger than $\pm 5\%$, the measurement should be repeated (DIN 2023).

The loaded sample carrier is removed from the sampling head, the capsule is sealed by screwing on its cap and then transported to the laboratory for analysis with as little jarring as possible.

5.2 Sample preparation

The samples are digested by microwave-assisted pressure digestion using hydrofluoric and nitric acid. As hydrofluoric acid is added, the containers used for digestion should be made of plastic.

Ceramic tweezers are used to transfer the loaded filters to the respective PTFE vials for microwave-assisted pressure digestion. 9 ml of 67–69% nitric acid (see Section 4.2) and 0.9 ml of 40% hydrofluoric acid are added. The vials are sealed with suitable PTFE caps and the filters are digested for 60 minutes at 240 °C (pressure approx. 60 bar). After cooling, the digestion solution is carefully transferred to a graduated 50-ml centrifuge tube (see Section 4.1) and the tube is filled to 20 ml with ultrapure water ($\rho \geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 °C). The solution is then prepared for ICP analysis.

Dilutions of the samples are prepared for quantitative analysis by placing aliquots of the digested sample into suitable graduated 15-ml PP vessels. A dispenser system is used to add 100 μl of the internal standard solution (400 $\mu\text{g Y/ml}$, see Section 4.4) and to fill the vessels to 10 ml with dilution solution.

A blank value is determined for each series of samples. For this purpose, at least two empty filters from the same batch are processed through all preparation and analysis steps of the method.

6 Operating conditions

Apparatus:	Quadrupole ICP mass spectrometer, NexION 350D, PerkinElmer LAS GmbH	
Plasma parameters:	Optimised for robust plasma conditions for samples/matrices of largely unknown composition ($\text{CeO/Ce} \leq 1.5\%$; $\text{Ce}^{++}/\text{Ce} \leq 1.5\%$) RF power: 1550 W	
Nebuliser:	Apex-ST PFA MicroFlow, 100–200 $\mu\text{l/min}$	
Nebuliser chamber:	Nebuliser with PFA Scott spray chamber	
Injector:	Quartz, inner diameter 2.0 mm	
Rinsing solution:	4.95 l of ultrapure water with 50 ml of 65% HNO_3	
Mobile phase:	495 ml of ultrapure water with 5 ml of 67–69% HNO_3	
Flow rate:	Sample solution:	0.4 ml/min
	Carrier gas:	1.07 l/min
	Auxiliary gas:	1.2 l/min
	Nebuliser gas flow rate:	15 l/min
Detector:	Secondary electron multiplier (SEM); dual stage detector	
Isotope:	Germanium 72 amu	
Measurement mode:	Standard	

Interference minimisation: Isobaric: not required
 Interference correction: not required
 Polyatomic: not required

Internal standard, isotope: Yttrium 89 amu

Measurement solutions: An aliquot of the sample solution is diluted to at least 1 : 10 (v/v). The internal standard solution is added using the same procedure as applied for the calibration standard (see Section 4.3). If the measurement results lie outside of the linear range of the calibration function, further dilutions, e.g. 1 : 100 and 1 : 1000 (v/v), must be prepared.

7 Analytical determination

After preparation, the diluted sample is continuously injected into the ICP mass spectrometer using an autosampler (0.4 ml/min) and analysed under the operating conditions described in Section 6.

8 Calibration

The calibration standards described in Section 4.4 are used to derive the calibration function.

The calibration standards are injected into the ICP mass spectrometer and analysed using the same procedure as the sample solutions. The quotient obtained by dividing the signal intensity of the peak area of germanium (A_{Ge}) by that of the internal standard yttrium (A_Y) is plotted against the germanium concentration of the calibration standards. The calibration function is linear over the examined range of concentrations (0.05–10 µg/l; Figure 1).

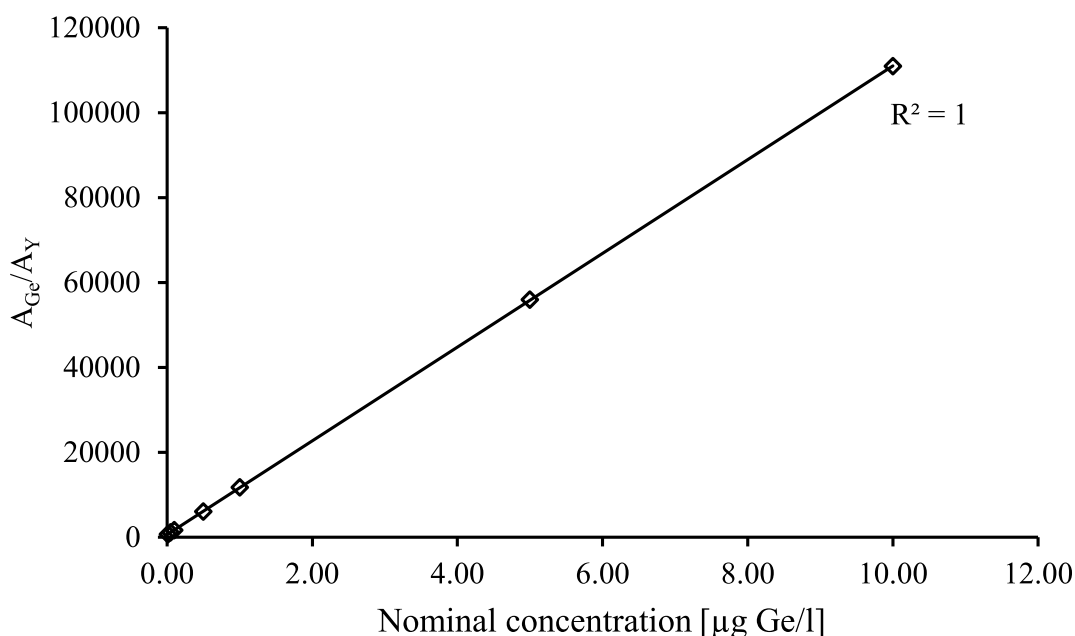


Fig. 1 Linear calibration function for germanium in the range 0.05–10 µg/l

To check the calibration function, control samples are analysed at the beginning and at the end of each series of measurements. The calibration must be performed every working day.

9 Calculation of the analytical result

The metal concentration in the workplace air is calculated based on the concentration of germanium that was determined by a data analysis programme in comparison with the internal standard in the measurement solution. The data analysis programme uses the determined calibration function for this purpose. The concentration of germanium in the workplace air is calculated (according to the same procedure as used for other metals) from the germanium concentrations taking the corresponding dilutions and the air sample volume into account. The concentration of analyte in the air is calculated using Equation 1.

$$\rho = \frac{(c - c_{blank}) \times 0.001 \times f_d \times V}{V_{air}} \quad (1)$$

where:

- ρ is the mass concentration of the substance in the air sample in mg/m³ at t_a and p_a
- ρ_0 is the mass concentration of the substance in mg/m³ at 20 °C and 1013 hPa
- c is the concentration of germanium in the measurement solution in µg/l
- c_{blank} is the concentration of the blank value (mean) in µg/l
- f_d is the dilution factor
- V is the volume of the sample solution in l
- V_{air} is the air sample volume in m³ (calculated from the volumetric flow rate and the sampling period)

10 Reliability of the method

The characteristics of the method were determined according to the standards DIN EN 482 (DIN 2021) and DIN EN ISO 21832 (DIN 2020). The limit of detection and quantification were determined according to DIN 32645 (DIN 2008). The software QMSys GUM Professional was used to carry out the uncertainty calculations (Qualisyst n.d.).

10.1 Precision and recovery

The recovery experiments included an assessment of reproducibility using the coefficient of variation (relative standard deviation) for the examined concentrations of germanium and germanium dioxide (see Table 3). For this purpose, the sampling parameters were assumed to be a two-hour sampling period at a volumetric flow rate of 10 l/min. The concentration was determined in a sample digestion volume of 20 ml. As aerosols of varying chemical composition and physical properties are found in different work areas, it is not possible to provide recovery data that are generally valid for the entire procedure. The analytical precision was not assessed because a coefficient of variation ≤5% was determined for reproducibility in all cases.

The method used for preparation and analysis was verified by means of a certified pure substance (germanium 99.999%, see Section 4.2) and a certified metal compound (germanium dioxide, anhydrous, see Section 4.2). Germanium concentrations of 0.085 mg/m³, 0.85 mg/m³ and 1.7 mg/m³ were included to cover the minimum measurement range. Recovery experiments were also carried out in the range of the determined limit of quantification to cover the limit of quantification and the range of the analytical procedure (see Table 3). In this experiment, not only recovery, but also the coefficient of variation for each concentration was calculated as a measure of reproducibility.

Recovery was determined by microwave-assisted pressure digestion. For this purpose, between 6 and 14 mg of the substances listed in Table 3 were weighed onto nitrocellulose filters (n=8). 9 ml of nitric acid (65%) and 0.9 ml of hydrofluoric acid (40%) were added to the loaded filters. The filters then underwent microwave-assisted pressure digestion under the operating conditions listed in Section 5.2. After cooling, the digested samples were transferred to

50-ml centrifuge tubes and the tubes filled to 20 ml with ultrapure water. The solutions prepared by this method did not contain any visible particles.

Eight reference solutions were obtained in this way. Each of these was used to prepare two intermediate dilutions with concentrations that were calculated to be 200 µg/l and 10 µg/l. The dilution scheme differed for each of the eight reference solutions because it was not possible to determine the exact mass. The first intermediate dilution (200 µg/l) was prepared by taking between 21 and 52 µl of the stock solution and adding dilution solution to obtain a total volume of 50 ml. The second intermediate dilution (10 µg/l) was prepared by taking 500 µl of the first intermediate dilution and adding dilution solution to obtain a total volume of 10 ml. The first intermediate dilution (200 µg/l) was used to determine the recovery within the minimum measurement range via three further dilution steps per sample. The second intermediate dilution (10 µg/l) was used to cover lower concentrations close to the limit of quantification of the method by means of one further dilution step.

In addition to the recovery samples, two unused filters (blank filters) were subjected to the complete analytical procedure and used for blank correction (see Section 9).

The quantitative analysis resulted in a mean recovery of 96.6% for germanium using the microwave-assisted pressure digestion method and of 97.9% for germanium obtained from germanium dioxide.

Tab. 3 Coefficients of variation for the reproducibility of germanium and germanium dioxide from recovery experiments with $n = 8$ determinations per concentration

Tested substance	Concentration of the intermediate dilution used [µg Ge/l]	Mass of Ge loaded onto the filter ^{a)} [mg]	Concentration Ge ^{b)} [mg/m ³]	Coefficient of variation [%]	Recovery [%]
Ge	10	0.004	0.000004	4.8	97.8
Ge	200	0.1	0.085	3.2	94.7
Ge	200	1.0	0.85	2.0	96.4
Ge	200	2.0	1.7	2.7	97.3
GeO ₂	10	0.004	0.000004	1.8	97.8
GeO ₂	200	0.1	0.085	5.0	96.9
GeO ₂	200	1.0	0.85	3.0	97.6
GeO ₂	200	2.0	1.7	1.6	99.3

a) The mass was not determined directly by weighing, but by reverse calculation after factoring in the dilution steps and the digestion volume.

b) The concentration is obtained for a sampling period of two hours at a volumetric flow rate of 10 l/min and a digestion volume of 20 ml.

10.2 Expanded uncertainty

The expanded uncertainty was determined by estimating all relevant influencing parameters. There are two main sources of uncertainty in the measurement results: the estimated uncertainties in the sampling procedure and those in the analytical procedure.

The uncertainties arising from sampling were estimated by determining the uncertainties associated with the air sample volume and the sampling effectiveness for the **inhalable** particle fraction according to Appendix C of the standard DIN EN ISO 21832 (DIN 2020). If the current method is used to determine the germanium content in the **respirable** particle fraction, the uncertainty assessment must take into account the specific uncertainties associated with sampling the respirable particle fraction (DIN 2020).

Uncertainties arising from analysis may occur at any point of the analytical procedure including digestion, dilution, calibration, recovery and precision. The QMSys GUM Professional software was used to determine the concentration-dependent analytical uncertainties for this method (Qualisyst n.d.).

The combined uncertainties for the entire method were calculated by combining the contributions from all sources of uncertainty. The percentages listed in Table 4 for the expanded uncertainty for the entire method for the tested germanium concentrations at a volumetric flow rate of 10 l/min and a sampling period of two hours were obtained by multiplying these values with the expansion factor $k = 2$.

Tab. 4 Expanded uncertainty U

Tested substance	Tested concentration [mg/m ³]	Expanded uncertainty (U) [%]
Ge	0.085	35.7
Ge	0.85	24.7
Ge	1.7	24.4

10.3 Influence of humidity

If the relative humidity exceeds 50% and if substances are present in the work area in dissolved form (droplet particles), it is recommended to load two quartz fibre filters into the filter cassette as sample carriers.

10.4 Limit of quantification

As the method was being developed, the limit of quantification was calculated using the equation given in the standard DIN 32645 (DIN 2008) by applying the blank value method on the basis of laboratory blank samples.

For this purpose, ten unused filters were processed through all preparation and analysis steps of the method (see Section 5.2). After analysis, the standard deviation of the signal and the mean signal value, the analyte blank values for all laboratory blank samples obtained from the filters, reagents and vessels used, and the analytical limit of quantification x_{LOQ} were determined as specified in DIN 32645 (see Equation 2). The slope of the calibration is also required.

$$x_{LOQ} \approx 10 \times \frac{s_{BV}}{b} \quad (2)$$

where:

x_{LOQ} is the limit of quantification in $\mu\text{g/l}$

s_{BV} is the standard deviation for replicate determinations of the blank value

b is the slope of the calibration function, which is also used during routine operations

The limit of quantification of the method was determined using Equation 3:

$$c_L = f_{st} \times f_d \times \frac{V_D}{V_{air}} \times x_{LOQ} \quad (3)$$

where:

c_L is the limit of quantification in air in mg/m^3

f_{st} is the conversion factor (stoichiometric factor)

f_d is the dilution factor

V_D is the digestion volume of the sample in ml

V_{air} is the air sample volume in m^3

10.5 Storage stability

The storage stability of the loaded sample carriers was analysed by spiking the filters with germanium in concentrations equivalent to 0.1 to 2 times the currently valid OELV.

Three sample carriers per concentration and storage day were spiked with the intermediate dilution single-element standard for germanium (see Section 4.3) to cover the lower concentration. To cover the upper concentration, three sample carriers each were spiked directly with the single-element standard for germanium (10 000 µg/ml, see Section 4.2). All sample carriers were dried at room temperature and then stored in the fume cupboard. These were prepared and analysed on two measurement days per week. The day after spiking is regarded as storage day 1.

Filters loaded with germanium in concentrations ranging from 0.085 mg/m³ to 1.7 mg/m³ are stable for up to four weeks. If the OELV for germanium is lowered, additional storage experiments with concentrations close to the limit of quantification must be carried out in order to ensure storage stability at lower concentrations.

Tab. 5 Comparative measurements for the storage of filters spiked with germanium in concentrations 0.1 and 2 times the currently valid OELV

Storage period [days]	Volume of spiking solution [µl]	Tested concentrations [mg/m ³]	Mean recovery [%]
32	100	0.085	100.9
32	200	1.7	101.9

10.6 Selectivity

Isobaric interferences must be avoided, if possible, by choosing other isotopes. Polyatomic interferences can largely be reduced by establishing robust plasma conditions (oxide rate and rate of doubly-charged ions $\leq 2\%$) as well as by applying the described collision cell technology followed by kinetic energy discrimination.

In samples of mainly unknown composition, high concentrations of other elements and compounds may still lead to interference. Therefore, the results of the analysis must generally be checked for possible interference (e.g. by determining several isotopes and modes). If necessary, a suitable dilution step must be chosen to achieve valid results.

In order to use the present method for determining germanium and its compounds, an isotope (Ge 72 amu) was chosen that does not cause isobaric interference. Interferences on germanium due to high concentrations of doubly-charged ⁷¹Ga⁺⁺-ions must be taken into consideration. Isotopes of this metal should be included in the analysis at least as monitor ions. The use of the standard mode (i.e. in the presence of ArCl) was found to be unproblematic for the determination of germanium. Therefore, a determination in KED (kinetic energy discrimination) mode does not need to be performed. Moreover, the calibration does not require correction for matrix effects.

11 Discussion

The measurement method described above provides a means of determining germanium and its compounds in the inhalable particle fraction in the workplace air in concentrations ranging from 0.1 to 2 times the currently valid OELV of 0.85 mg/m³. As germanium typically occurs in lower concentrations at the workplace, the calibration was adjusted (in the range of 0.05–10 µg/l or 0.008–1.7 µg/m³). Furthermore, recovery experiments at the limit of quantification ensure that the results obtained using this method are reliable also for lower concentrations. The storage stability of carriers spiked with concentrations close to the limit of quantification needs to be examined if sample carriers cannot be processed immediately. If necessary, samples with higher concentrations should be diluted to this concentration range. The method is also suitable for monitoring compliance with the short-term value.

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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