

Cadmium – Method for the determination of cadmium and its compounds in workplace air using graphite furnace atomic absorption spectrometry (GF-AAS) after high-pressure microwave digestion

Air Monitoring Method

Keywords

cadmium; air analyses; analytical method; workplace measurement; hazardous substance; GF-AAS; high-pressure microwave digestion; atomic absorption spectrometry

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Abstract

This analytical method is a validated measurement procedure for the determination of cadmium [7440-43-9] and cadmium compounds in workplace air after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a quartz fibre filter using a suitable flow-regulated pump. After high-pressure microwave digestion, the respirable and inhalable fraction of cadmium retained on the filter is analysed using an atomic absorption spectrometer with the graphite furnace technique. The relative limit of quantification (LOQ) is 0.0019 µg cadmium/m³ for an air sample volume of 1.2 m³. Sampling is performed over 2 h at a flow rate of 10 l/min, a

measurement solution volume of 25 ml and an injection volume of 20 µl. It is not possible to differentiate between the individual cadmium compounds. The mean recovery for cadmium was 100%. The concentration-dependent expanded uncertainty was between 26 and 27% and the concentration-dependent uncertainty for the determination of cadmium in the inhalable fraction was 26 to 27%, too. 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 cadmium 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-Nr.	Molar mass	Formula	Substance-specific concentration values
		[g/mol]		[µg Cd/m ³]
Cadmium and inorganic cadmium compounds (as cadmium), classified as C1A and C1B	7440-43-9	112.41	Cd	TC 2.0 (R) EF 8 (AGS 2022 b) AC 0.9 (R) (AGS 2022 b)
Cadmium and inorganic cadmium compounds (as cadmium)	7440-43-9	112.41	Cd	OELV 2.0 (I) EF 8 (II) (AGS 2022 a)

AC: acceptable concentration; EF: excursion factor, short-term value in parentheses; I: inhalable fraction; OELV: occupational exposure limit value; R: respirable fraction; TC: tolerable concentration

1 Summary

The mean concentration of cadmium and its compounds (as cadmium) 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 quartz fibre filter. After high-pressure microwave digestion, the respirable and inhalable fraction of cadmium retained on the filter is analysed using an atomic absorption spectrometer with the graphite furnace technique.
Limit of quantification (calculated as Cd):	Absolute: 1.8 pg of cadmium 0.0023 µg of cadmium per sample carrier Relative: 0.0019 µg/m ³ for an air sample volume of 1.2 m ³ (a sampling period of 2 h at 10 l/min, a measurement solution volume of 25 ml and an injection volume of 20 µl)
Measurement range:	0.0019 to 0.167 µg/m ³ based on an air sample volume of 1.2 m ³ and 0.06 to 23.8 µg/m ³ based on an air sample volume of 420 l.
Selectivity:	Interference by other components was not observed. Possible matrix effects can be corrected by measurement with Zeeman correction and by calibration of the sample in accordance with the standard addition method. It is not possible to differentiate between the individual cadmium compounds.
Advantages:	It is possible to conduct personal sampling with great sensitivity and to determine other analytes in the sample solution with the atomic spectrometric parameters adapted accordingly.
Disadvantages:	No indication of concentration peaks, requires great technological resources.

Apparatus: Sampling devices:
Pump and sampling head, filter holder with quartz fibre filter and supporting sieve
Flow meter
High-pressure microwave digestion system
Atomic absorption spectrometer with graphite furnace technique

2 Equipment and chemicals

2.1 Equipment

For sampling:

- Pump, suitable for a flow rate of 3.5 to 10 l/min (e. g. SG10-2, from GSA, Gesellschaft für Schadstoffanalytik mbH, 40880 Ratingen, Germany)
- PGP system with FSP 10 sampling head, suitable for a flow rate of 10 l/min, from DEHA, Haan & Wittmer, 71296 Heimsheim, Germany
- GSP sampling head, suitable for a flow rate of 3.5 l/min, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany
- Filter holder and cap made of PTFE with supporting sieve
- Quartz fibre filter, diameter 37 mm (e. g. QM-A from Whatman, supplied by VWR, 64295 Darmstadt, Germany)
- Gas flow meter (e. g. rotameter flow meter, influx 1 to 13 litres, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany)

For the sample preparation and the analytical determination:

- Atomic absorption spectrometer with graphite furnace technique, autosampler and cadmium hollow cathode lamp
- High-pressure microwave digestion system (e. g. MarsXpress with digestion vessels and seals made of PTFE, from CEM, 47475 Kamp-Lintford, Germany)
- Analytical balance
- Plastic tweezers
- Variable piston pipettes 1 to 50 000 µl (e. g. Multipette pro, from Eppendorf, 22339 Hamburg, Germany)
- Volumetric flasks, 10 ml, 25 ml and 50 ml, made of DURAN glass
- Glass funnel (e. g. 55 mm diameter)
- Wide-necked flasks, 50 ml made of PE
- Disposable syringes, 5 ml made of PE
- Syringe filters made of regenerated cellulose, pore width 0.45 µm, diameter 30 mm (e. g. from Roth, 76185 Karlsruhe, Germany)
- Autosampler vials made of PE or PTFE

2.2 Chemicals

- Nitric acid, 65%, with a low metal content (e. g. Suprapur, from Merck KGaA, 64293, Darmstadt, Germany)
- Hydrochloric acid, 30%, with a low metal content (e. g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)

- Water for trace analysis, with a low metal content (e.g. Tracepur, from Merck KGaA, 64293 Darmstadt, Germany)
- Magnesium nitrate hexahydrate, with a low metal content (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Ammonium dihydrogen phosphate, with a low metal content (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Cadmium standard for the AAS with a certified cadmium content of 1000 mg/l in diluted nitric acid, traceable to a standard reference material (e.g. from Merck KGaA, 64293 Darmstadt, Germany, Order No. 1.19777)
- Multi-element Standard Solution 4 for ICP, with a certified cadmium content of 10 mg/l in diluted nitric acid, traceable to a standard reference material (e.g. from Merck KGaA, 64293 Darmstadt, Germany, Order No. 51844)
- Argon 5.0 (purity at least 99.999%)

2.3 Solutions

Note: Before use, all glassware must be pre-rinsed with dilute nitric acid and then rinsed with water for trace analysis, in order to ensure that all vessels are free of any metal traces.

Modification solution: Solution of 0.6 g magnesium nitrate/l and 10 g ammonium dihydrogen phosphate/l in water
Approx. 26 mg of magnesium nitrate hexahydrate and 303 mg of ammonium dihydrogen phosphate are weighed out and transferred into the 25 ml volumetric flask, into which water has been previously placed. The volumetric flask is filled to the mark with water and shaken.

Blank value solution: Solution of 0.65% nitric acid in water

0.1 ml of nitric acid (65%) is pipetted into a 10 ml volumetric flask, into which approx. 5 ml of water have been previously placed. The volumetric flask is filled to the mark with water and shaken.

Calibration Solution 1: Solution of 2.5 mg cadmium/l water

Water is placed into a 50 ml volumetric flask. 125 µl of the cadmium standard (1000 mg Cd/l) are pipetted into the volumetric flask, the flask is then filled to the mark with water and shaken.

Calibration Solution 2: Solution of 0.125 mg cadmium/l water

Water is placed into a 25 ml volumetric flask. 1.25 ml of Calibration Solution 1 are pipetted into the volumetric flask, which is then filled to the mark with water and shaken.

Calibration Solution 3: Solution of 2.5 µg cadmium/l water

In order to stabilise the dilution, 0.25 ml of nitric acid (65%) is pipetted into a 25 ml volumetric flask, into which water has been previously placed. Then 500 µl of Calibration Solution 2 are pipetted into the volumetric flask, which is then filled to the mark with water and shaken. This solution is stable for a period of at least two weeks.

Control Solution 1: Solution of 0.2 mg cadmium/l water

Water is placed into a 25 ml volumetric flask. 50 µl of Multi-element Standard Solution 4 (10 mg Cd/l) are pipetted into the volumetric flask, which is then filled to the mark with water and shaken.

Control Solution 2: Solution of 2 µg cadmium/l water

In order to stabilise the dilution, 0.25 ml of nitric acid (65%) is pipetted into a 25 ml volumetric flask, into which water has been previously placed. Then, 0.25 ml of Control Solution 1 is pipetted into the volumetric flask, which is then filled to the mark with water and shaken. This solution is stable for a period of at least two weeks.

Cadmium Solution 1: Solution of 5 mg cadmium/l water

In order to stabilise the dilution, 0.1 ml of nitric acid (65%) is pipetted into a 10 ml volumetric flask, into which water has been previously placed. 50 µl of the cadmium standard (1000 mg Cd/l) are pipetted into the volumetric flask, the flask is then filled to the mark with water and shaken.

3 Sampling

The filter batch used must be checked for its suitability before measurements (see [Section 5.2](#)).

Sampling can be carried out as stationary or personal sampling. The caps of the filter transport capsules are removed and a quartz fibre filter (Ø 37 mm) with a supporting sieve is placed into the FSP sampling system. A membrane filter is also suitable for use. A flow rate of 10 l/min is then set. This is equivalent to an air sample volume of 1200 l for a sampling period of 2 hours. After sampling, the flow rate must be checked for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to repeat the measurement (see DGUV Information 213-500 “General Part”, Section 3 (DGUV 2015)).

The GSP sampling head with a flow rate of 3.5 l/min can also collect the inhalable particle fraction in the same manner as the respirable particle fraction. This is equivalent to an air sample volume of 420 l for a sampling period of 2 hours. Alternatively, the sampling head can also be used with a suitable intake cone for a flow rate of 10 l/min.

A blank sample (field blank value) is included in addition to the samples. This serves as a transport check and differs from the analytical sample in that no sample air is drawn through the filter.

The loaded filters are then removed from the sampling system and sealed with the caps for the transport capsules.

4 Analytical determination

4.1 Sample preparation

The loaded filters and the field blank are each transferred into a separate digestion vessel using plastic tweezers and 6 ml of nitric acid (65%) and 3 ml of hydrochloric acid (30%) are added to each vessel. The vessels are covered with the caps and sealed with the screw-caps. These are then evenly distributed on the sample turntable of the microwave digestion device and the dust deposited on the filters is digested.

Digestion is carried out by increasing the microwave power to 800 W within a period of 10 minutes and maintaining it at this level for 10 minutes. The maximum permissible control temperature is around 210 °C. After the sample has been digested, it is left to cool in the microwave device. In this case, the quartz fibre filter is not digested completely.

Water with a low metal content is used to quantitatively transfer the digestion solution into a 25 ml volumetric flask through a previously cleaned glass funnel. The volumetric flask is filled to the mark and shaken. The sample solution is transferred into a 50 ml wide-necked flask made of PE for storage. If precipitation occurs or there are non-soluble components, then the sample solution is filtered using a disposable syringe filter. Immediately before analysis, part of the sample solution is transferred into an autosampler vial. A suitable pre-dilution is carried out, if required.

If the cadmium concentration of the field blank value is above that of the batch blank value and the limit of quantification, then an additional batch blank value, a non-loaded filter from the same batch in the laboratory, must be prepared and analysed.

The prepared samples, field blank and batch blank are injected into the AAS by means of the autosampler and analysed.

4.2 Operating conditions

AAS parameters:	Graphite furnace AAS with autosampler (PerkinElmer PinAAcle 900Z with Zeeman background compensation and transversely heated graphite tube including a L'vov platform) Cadmium hollow cathode lamp, warm-up period at least 15 minutes
Wavelength:	228.8 nm
Slit width:	0.7 nm
Injection:	20 µl of the sample solution + 5 µl of the modification solution + 5 µl of the blank value solution (injection in duplicate in each case)

Tab.1 Oven program

Step	Temperature [°C]	Heating period [s]	Dwell time [sec]	Gas flow rate [ml/min]
Drying 1	120	1	30	250
Drying 2	140	15	40	250
Pyrolysis	700	10	20	250
Atomisation	1500	0	3	0
Heating	2450	1	3	250

The prepared samples, the field blank value, a reagent blank value consisting of nitric acid and hydrochloric acid at a ratio of 2:1 (analogous to the digestion), the blank value solution and, if necessary, a filter batch blank value are analysed in the AAS. For this purpose, 20 µl each of the solution to be investigated with 5 µl of the blank value solution and 5 µl of the modification solution are injected into the AAS using the autosampler and analysed under the specified AAS operating conditions. Each sample is analysed twice and the mean value is used to calculate the result.

The sample solutions are diluted with water and nitric acid (65%), if the cadmium concentrations are above the range of the calibration curve, so that there is an acid level of at least 0.65% in the dilution for the purpose of stabilisation. The dilution factor can be estimated by means of pre-analyses.

The blank value is checked regularly by measuring the blank value solution, at the latest after every eighth sample, and the signal (area) is adjusted to zero.

Control Solution 2 is analysed before analysis of the sample solution and at the end of the sequence. The concentration must fall within defined limits (in this case $\pm 10\%$), otherwise the calibration must be checked and analysis of the sample solution must be repeated. This serves to check the stability of the analytical devices and the accuracy of the results. In the case of larger sample series, it is advisable to carry out further periodic measurements of Control Solution 2.

A possible matrix influence must be checked at least once per sample series. For this purpose, at least one sample is analysed anew and 5 µl of the blank value solution is replaced by 5 µl of Calibration Solution 3. The recovery is calculated from the cadmium concentration of the spiked sample after deduction of the cadmium concentration of the original sample in relation to the spiked cadmium concentration. This must be between 90 and 110%, otherwise a matrix effect must be assumed. In this case, it is important to ensure that the spiked sample is within the range of the calibration curve.

Example: A cadmium concentration of the sample solution of 1.5 µg/l, a cadmium concentration of the spiked sample of 2.2 µg/l and a spiked cadmium concentration of 0.625 µg/l results in a recovery of 104% (calculated from: $2.2 / (1.5 + 0.625) \times 100$).

If the matrix of the sample has a significant influence, evaluation using the standard addition method with the sample solution is required.

5 Evaluation

5.1 Calibration

5.1.1 External calibration

The calibration must be performed every working day. Calibration Solution 3 with a concentration of 2.5 µg/l of cadmium is diluted by the autosampler as specified in the following scheme (see [Table 2](#)) to yield the six calibration standards. Additionally, 5 µl of the modification solution are also added by the autosampler in the same manner as for the samples. The standards are analysed under the AAS operating conditions described in [Section 4.2](#) and a linear calibration function is obtained.

Tab.2 Calibration standards for external calibration

	Concentration [µg Cd/l]	Blank value solution [µl]	Calibration Solution 3 [µl]
Cadmium blank value	0	25	0
Calibration Standard 1	0.25	23	2
Calibration Standard 2	0.75	19	6
Calibration Standard 3	1.25	15	10
Calibration Standard 4	1.75	11	14
Calibration Standard 5	2.25	7	18
Calibration Standard 6	2.75	3	22

Control Solution 2 is analysed in order to check the calibration (see [Section 4.2](#)).

5.1.2 Standard addition calibration

In order to eliminate a possible matrix effect, the sample must undergo a standard addition calibration. The cadmium concentration of the sample should be between 1 and 2.75 µg/l. The calibration standards are obtained by addition of different concentrations of Calibration Solution 3 to the sample (see [Table 3](#)). For this calibration, 5 µl of the modification solution are also pipetted into the standard using the autosampler. All standards and solutions are analysed in duplicate.

Otherwise, the AAS operating conditions remain unaltered.

The intercept of the calibration curve with the x-axis is equivalent to the cadmium concentration of the sample solution.

Tab. 3 Standard addition calibration

	Concentration [µg Cd/l]	Blank value solution [µl]	Sample solution [µl]	Calibration Solution 3 [µl]
Cadmium blank value	0	25	0	0
Sample		15	10	0
Calibration Standard 1	1	11	10	4
Calibration Standard 2	1.75	8	10	7
Calibration Standard 3	2.5	5	10	10

5.2 Calculation of the analytical result

The cadmium concentration c in the air sample in $\mu\text{g}/\text{m}^3$ is obtained as follows (see Equation 1):

$$c = \frac{((c_{\text{SOL}} \times F) - c_{\text{FB}}) \times V_{\text{SOL}}}{1000 \times \eta \times V} \quad (1)$$

where:

c is the mass concentration of cadmium in the air sample in $\mu\text{g}/\text{m}^3$

c_{SOL} is the concentration of cadmium in the measurement solution in $\mu\text{g}/\text{l}$ obtained from the calibration curve

c_{FB} is the concentration of cadmium in the measurement solution of the field blank value in $\mu\text{g}/\text{l}$ obtained from the calibration curve

F is the dilution factor

V_{SOL} is the volume of the prepared sample solution in ml (= 25)

V is the air sample volume in m^3

η is the recovery (1.0, 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 2021) and DIN 32645 (DIN 2008).

6.1 Repeatability

The repeatability was determined by analysing one standard solution (prepared from Cadmium Solution 1) and one prepared sample on six different days. Calibration was carried out every working day for quantification. The cadmium concentration of both the solutions was $8 \mu\text{g}/\text{l}$, therefore instead of $20 \mu\text{l}$ of the sample solution $5 \mu\text{l}$ were injected, in order to enable evaluation within the range of the curve. The repeatability of the standard solution was 4.1% and that of the sample 5.4%.

6.2 Reproducibility and 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 recovery was determined by spiking 12 quartz fibre filters each with $40 \mu\text{l}$ of Cadmium Solution 1 ($5 \text{ mg}/\text{l}$). Six filters were prepared and analysed as described in Section 4.1 and 4.2. Laboratory air was drawn through the other six filters over a time period of 2 hours at a flow rate of $10 \text{ l}/\text{min}$. These were then also prepared and analysed.

In order to obtain reference values, a pipette was used to add 40 µl of Cadmium Solution 1 (5 mg/l) each into six 25 ml volumetric flasks, into which water and 0.25 ml of 65% nitric acid had been previously placed. The solutions were filled to the mark with water, shaken and analysed according to [Section 4.2](#)

The cadmium concentrations of the spiked filters were calculated in relation to the reference values and on this basis the analytical recovery (conversion) and the recovery with air sampling were determined. The analytical recoveries thus obtained as well as the recovery with sampling were not statistically significantly different from the reference values according to the *t*-test and are taken into account for calculation of the result with $\eta=1$.

The spiked amount of cadmium was equivalent to the concentration in the air sample listed in [Table 4](#) for an air sample volume of 1.2 m³. The reproducibility, expressed as the relative standard deviation, was determined from the six spiked filters with air sampling and was around 1%.

Tab.4 Characteristics of the validation

Spiked volume per filter	Spiked mass per filter	Concentration in the air sample	Conversion	Recovery	Relative standard deviation
[µl]	[µg]	[µg/m ³]			[%]
40	0.2	0.167	0.97	0.99	1.0

Recovery experiments with a spiked mass of 10 µl of Cadmium Standard (1000 mg/l) and an air sample volume of 420 l resulted in a statistically non-significant recovery of 0.96 and a reproducibility of 6.3% (see [Table 5](#)).

Tab.5 Characteristics of the validation at high concentrations

Spiked volume per filter	Spiked mass per filter	Concentration in the air sample	Conversion	Recovery	Relative standard deviation
[µl]	[µg]	[µg/m ³]			[%]
10	10	23.8	1.0	0.96	6.3

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

6.3 Limit of quantification

As the filters show no evidence of cadmium blank values, the absolute limit of quantification was determined using a calibration curve in the lower concentration range as stipulated in DIN 32645 (DIN 2008). For this purpose, Calibration Solution 3 with a concentration of 2.5 µg/l is diluted by the autosampler to yield the ten calibration standards as specified in the following scheme (see [Table 6](#)). Additionally, 5 µl of the modification solution are also added by the autosampler in the same manner as for the samples. The standards and the blank values are analysed under the AAS operating conditions as described in [Section 4.2](#) and a linear calibration function is obtained.

Tab.6 Calibration standards for the external calibration for determination of the limit of quantification

	Concentration	Blank value solution	Cadmium Solution 3
	[µg Cd/l]	[µl]	[µl]
Cadmium blank value	0	25	0
Calibration Standard 1	0.125	24	1
Calibration Standard 2	0.250	23	2
Calibration Standard 3	0.375	22	3

Tab. 6 (continued)

	Concentration [µg Cd/l]	Blank value solution [µl]	Cadmium Solution 3 [µl]
Calibration Standard 4	0.500	21	4
Calibration Standard 5	0.625	20	5
Calibration Standard 6	0.750	19	6
Calibration Standard 7	0.875	18	7
Calibration Standard 8	1.000	17	8
Calibration Standard 9	1.125	16	9
Calibration Standard 10	1.250	15	10

The absolute limit of quantification is 0.09 µg/l or 1.8 pg of cadmium per injection for a statistical certainty of 95% and a relative uncertainty of the result of 33% or $k = 3.33$.

A relative limit of quantification of 0.0019 µg/m³ of cadmium or 0.0023 µg of cadmium per sample carrier is obtained for an air sample volume of 1.2 m³, a sample solution volume of 25 ml and an injection volume of 20 µl.

6.4 Storage stability

Cadmium deposited on a filter can be stored at room temperature without losses for at least 22 days. Storage stability of a prepared sample solution with a concentration of approx. 8 µg Cd/l is at least 40 days at room temperature.

6.5 Selectivity

High concentrations of other elements and compounds can lead to interferences. In principle, for samples of unknown composition, the measurement results must be checked for possible interferences and, if necessary, a suitable dilution step must be selected in order to achieve a valid result. Non-spectral interferences and matrix effects can be reduced by means of a suitable dilution. Non-spectral matrix effects can also be effectively eliminated by use of the Zeeman correction.

To date, interferences due to other components, in particular at high concentrations, have not been observed, however, these cannot be ruled out. Possible matrix effects can be eliminated by calibration of the sample solution in accordance with the standard addition method. It is not possible to differentiate between the individual cadmium compounds.

6.6 Uncertainty

The expanded uncertainty is obtained by estimation of all the relevant influencing parameters (bottom-up method). The uncertainty of the result consists principally of the uncertainty contributions of sampling u_s and the analytical preparation (preparation volume u_v , dilution of the sample solution u_D , recovery and storage losses u_R , concentration-dependent influences of the measurement values u_{MV} attributable to the scatter of the calibration function, uncertainty of the calibration solution and the laboratory's own reproducibility).

The combination of all uncertainty contributions results in the concentration-dependent combined uncertainty u_{comb} . The corresponding expanded uncertainty that represents the concentration-dependent uncertainty of the entire procedure is obtained by multiplication with a probability factor ($k = 2$ for 95% confidence level).

The estimation of the sampling-dependent components of the uncertainty is based on the following factors according to Annex B of DIN EN ISO 21832 (DIN 2020) for sampling respirable dusts:

Calibration of the test system:	1%
Estimation of the aggregated concentration:	1%
Systematic deviation from the sampling convention:	8%
Deviation from the nominal flow of the cyclone:	3%
Individual variability of the sampling device:	7%

This results in a combined uncertainty for the sampling system of 11.1%.

A combined uncertainty for sampling respirable dusts u_s of 11.7% is obtained taking a sampling period of 120 minutes into account.

The individual uncertainty contributions and the resulting combined uncertainties are summarised in [Table 7](#).

Tab. 7 Uncertainty contributions in % for cadmium determination in the respirable particle fraction

u_s	u_v	u_D	u_R	u_{MV}		u_{comb}	
				C_1 (1 $\mu\text{g Cd/l}$)	C_2 (2.5 $\mu\text{g Cd/l}$)	C_1	C_2
11.7	0.1	0.75	2.1	6.1	5.9	13.4	13.2

[Table 8](#) lists the concentration-dependent expanded uncertainties u_{exp} with the corresponding cadmium concentrations of the sample solution and the relevant cadmium concentrations in the air at an air sample volume of 1.2 m³ with and without dilution. Only the uncertainties for the medium to higher calibration range were taken into account, as at higher cadmium concentrations in the air the samples in this calibration range are diluted.

Tab. 8 Expanded concentration-dependent uncertainties

	C_1	C_2
Expanded uncertainty [%]	27	26
Cadmium concentration in the sample solution [$\mu\text{g/l}$]	1	2.5
Cadmium concentration in the air [$\mu\text{g/m}^3$]	0.021	0.052
Cadmium concentration in the air with a sample diluted by a factor of 10 [$\mu\text{g/m}^3$]		0.52

In order to calculate the expanded uncertainty for the determination of cadmium in the inhalable particle fraction the uncertainty components of sampling were estimated according to Appendix B in DIN EN ISO 21832 (DIN 2020).

Calibration of the test system:	0.5%
Estimation of the aggregated concentration:	4%
Systematic deviation from the sampling convention:	7.5%

This results in a combined uncertainty for the sampling system of 8.5%.

The results of the recovery with the high spiked quantity were taken into account to calculate the combined uncertainty. [Table 9](#) lists the concentration-dependent expanded uncertainties u_{exp} with the corresponding cadmium concentrations of the sample solution and the respective cadmium concentrations in the air at an air sample volume of 0.42 m³ with and without dilution.

Tab. 9 Expanded concentration-dependent uncertainties for the determination of cadmium in the inhalable particle fraction

	C ₁	C ₂
Expanded uncertainty [%]	27	26
Cadmium concentration in the sample solution [$\mu\text{g/l}$]	1	2.5
Cadmium concentration in the air [$\mu\text{g/m}^3$]	0.06	0.15
Cadmium concentration in the air with a sample diluted by a factor of 20 [$\mu\text{g/m}^3$]	1.2	3.0

6.7 Comparative measurement

In 2017, as part of an interlaboratory comparability experiment, the high-pressure microwave digestion described here was compared to an open digestion method published by the MAK Commission (Pitzke et al. 2020). For this purpose, a grinding dust was weighed onto a nitrocellulose filter, prepared and analysed. The cadmium concentration of the dust for the open digestion was 0.002% on average with a relative standard deviation of 9.2% for six participating laboratories. A concentration of 0.0019% was determined with the analytical method described here. Comparability between the high-pressure microwave digestion described here and the open digestion is thus confirmed.

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.

References

- AGS (Ausschuss für Gefahrstoffe) (2022 a) Technische Regeln für Gefahrstoffe (TRGS 900). Arbeitsplatzgrenzwerte. Dortmund: BAuA. https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-900.pdf?__blob=publicationFile&v=4, accessed 13 Oct 2022
- AGS (Ausschuss für Gefahrstoffe) (2022 b) Technische Regeln für Gefahrstoffe (TRGS 910). Risikobezogenes Maßnahmenkonzept für Tätigkeiten mit krebserzeugenden Gefahrstoffen. Dortmund: BAuA. https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-910.pdf?__blob=publicationFile&v=3, accessed 13 Oct 2022
- DGUV (Deutsche Gesetzliche Unfallversicherung), editor (2015) DGUV Information 213-500 Allgemeiner Teil. Von den Unfallversicherungsträgern anerkannte Analyseverfahren zur Feststellung der Konzentration krebserzeugender, erbgutverändernder oder fortpflanzungsgefährdender Stoffe in der Luft in Arbeitsbereichen. Berlin: DGUV. <http://publikationen.dguv.de/dguv/pdf/10002/213-500.pdf>, accessed 06 May 2021
- DIN (Deutsches Institut für Normung), editor (2008) DIN 32645:2008-11. Chemische Analytik – Nachweis-, Erfassungs- und Bestimmungsgrenze unter Wiederholbedingungen – Begriffe, Verfahren, Auswertung. Berlin: Beuth. <https://doi.org/10.31030/1465413>
- DIN (Deutsches Institut für Normung), editor (2020) DIN EN ISO 21832:2020-08. Workplace air – Metals and metalloids in airborne particles – Requirements for evaluation of measuring procedures (ISO 21832:2018); English translation of German version EN ISO 21832:2020. Berlin: Beuth. <https://doi.org/10.31030/3157765>
- DIN (Deutsches Institut für Normung), editor (2021) DIN EN 482:2021-05. Workplace exposure – Procedures for the determination of the concentration of chemical agents – Basic performance requirements; English translation of German version EN 482:2021. Berlin: Beuth. <https://doi.org/10.31030/3211072>
- Pitzke K, Breuer D, Hebisch R, Kirchner M, Maschmeier C-P, Mattenklott M, Schmitz A, Schuh C, Schwank T, Sonnenburg R, Timm K, Brock TH, Hartwig A, MAK Commission (2020) Determination of metal-containing components of airborne particles. Air Monitoring Method – Translation of the German version from 2019. MAK Collect Occup Health Saf 5(4): Doc091. https://doi.org/10.34865/amdetercompegt5_4or