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Method for the determination of cadmium and its inorganic compounds in workplace air using ICP mass spectrometry

Air Monitoring Method

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Abstract

This analytical procedure is a validated measurement method for the determination of cadmium and its inorganic compounds in workplace air averaged over the sampling period after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a membrane filter located in the sampling head (GSP and FSP) of the sampling device using a suitable flow-regulated pump. The flow rate is set to 10 L/min with a recommended air sample volume of 1200 L. The collected cadmium is prepared by unpressurised acid digestion and analysed by means of mass spectrometry with inductively coupled plasma (ICP-MS). The quantitative determination is based on a calibration function obtained by means of an equidistant 10-point calibration. The absolute limit of quantification (LOQ) is 0.1 µg/L and the relative LOQ is 0.007 µg/m^3 based on an air sample volume of approx. 1.2 m^3. The mean recovery is 102% and the expanded uncertainty for cadmium in inhalable dusts is approx. 19% and approx. 26% in respirable dusts.

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Keywords

cadmium; cadmium acetate; cadmium chloride; cadmium oxide; cadmium sulphate; cadmium sulphide; inductively coupled plasma; mass spectrometry; ICP-MS; FSP sampling head; GSP sampling head; acid digestion; air analysis; analytical method; workplace measurement; hazardous substances

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Method for the determination of cadmium and its inorganic compounds in workplace air using ICP mass spectrometry after acid digestion

German Social Accident Insurance
Expert Committee Raw Materials and Chemical Industry
Subcommittee Hazardous Substances

Analytical Subcommittee of the Chemistry Board of Experts[1)]

Recognised analytical procedures for the determination of carcinogens, mutagens or substances toxic to reproduction

Order number: DGUV Information 213-554 Method 02 Issued: December 2015

This method has been tested and recommended for the determination of cadmium and its inorganic compounds in the air at workplaces by the German Social Accident Insurance.

Both personal and stationary sampling can be performed for risk assessment at work.

Sampling is carried out with a pump and collection on a particulate filter. Analysis is performed by ICP mass spectrometry after acid digestion.

In the justification for the exposure-risk relationship (ERR) for cadmium published in the TRGS 910 [1] the following technically relevant hazardous substances are listed:

Name	CAS number
Cadmium	7440-43-9
Cadmium acetate	543-90-8
Cadmium chloride	10108-64-2
Cadmium oxide	1306-19-0
Cadmium sulphate	10124-36-4
Cadmium sulphide	1306-23-6

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Summary

This analytical method describes the determination of the mean concentration of cadmium and its inorganic compounds in workplace air averaged over the sampling period after personal or stationary sampling.

Principle: A pump draws a defined volume of air through a nitrocellulose membrane filter. After unpressurised acid digestion, the aerosol captured on the collection phase is analysed by means of mass spectrometry with inductively coupled plasma (ICP-MS).

Limit of quantification: (calculated as Cd)
The limit of quantification is essentially influenced by the collection phase used.

a) Use of commercially available nitrocellulose membrane filters:

absolute: 6 µg/L

relative: 0.5 µg/m³ at an air sample of 1.2 m³ (2 h of sampling at an intake rate of 10 L/min)
0.13 µg/m³ at an air sample of 4.8 m³ (8 h of sampling at an intake rate of 10 L/min)
as well as a measuring solution of 20 mL and a dilution factor of 5

b) Use of batch-tested nitrocellulose membrane filters:

absolute: 0.1 µg/L

relative: 0.007 µg/m³ at an air sample of 1.2 m³ (2 h of sampling at an intake rate of 10 L/min)
as well as a measuring solution of 20 mL and a dilution factor of 4

Selectivity: Molybdenum contained in the samples can, particularly in the case of a high oxide formation rate in the plasma, lead to elevated measured values. Identification of individual cadmium compounds is not possible with this method. The selectivity of the method depends above all on the selection of the isotopes, the absence of spectral interference and the minimisation of non-spectral interference. In the case of the principally unknown samples the measurement results must be checked for possible relevant interferences and, if necessary, a suitable dilution step must be chosen in order to achieve a valid result.
Numerous polyatomic interferences can be minimised by the use of collision or reaction cell technology. Isobaric interferences should be avoided by selection of alternative isotopes if possible.
The conditions stated here have proved successful in practice.

Advantages: Personal measurements with high sensitivity are possible; if necessary simultaneous determination of further analytes.

Disadvantages: Involves the use of costly equipment and is logistically complicated. High concentrations of other elements and compounds can lead to interferences. The absence of relevant interferences must be checked by qualified personnel.

Apparatus: Sampling system consisting of a pump and sampling head, filter holder with particle filter, flow meter, digestion apparatus and ICP-MS system.

Detailed description of the method

Inhaltsverzeichnis

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

- Pump, suitable for a flow rate of 10.0 L/min, e.g. SG10-2, from GSA Gesellschaft für Schadstoffanalytik GmbH, 40880 Ratingen, Germany
- GSP sampling head, adjusted for a flow rate of 10 L/min, from GSA

- FSP sampling head, adjusted for a flow rate of 10 L/min, from GSA
- Nitrocellulose membrane filter, pore size 8 µm, ∅ 37 mm, e.g. MF 11301 from Sartorius AG, 37075 Göttingen, Germany
- Flow meter, e.g. Gilibrator II from Gilian supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany

For sample preparation and analytical determination:

- ICP mass spectrometer, if appropriate with autosampler
  (the use of a dynamic reaction or collision cell is not strictly necessary, however, its omission can lead to false positive results, in the presence of certain matrix components, see Section 5.4)
- Nebulisation chamber made of quartz or PFA, if appropriate with Peltier cooling
- Nebuliser, e.g. concentric nebuliser, preferably made of PFA
- Graduated digestion cylinder (nominal volume of 25 mL, increments of 0.2 mL, precision class A or B) made of quartz glass and standardised inner ground glass joint NS 19/26 (the blank value must be separately checked before each use.)
- Sealing caps for digestion vessels (e.g. made of PE)
- Glass rods (e.g. quartz glass rods that have replaceable PTFE tube pieces to fit on the tips)
- Air cooler made of quartz glass (length approx. 30 – 40 cm) with standardised outer and inner ground glass joints NS 19/26
- Metal block thermostat with removable heating blocks with suitable drilled holes to accommodate digestion vessels, working range up to 200 °C
- Disposable vials (PP) with conical bottom and screw caps, 15 and 50 mL, suitable for the autosampler used
- Ceramic tweezers
- Disposable pipettes made of plastic, 5 mL, graduated
- Variable volume pipettes, 0.5 – 10 µL, 10 – 100 µL, 100 – 1000 µL and 500 – 2500 µL (e.g. Transferpette® from BRAND GmbH & Co. KG, 97877 Wertheim or Reference® from Eppendorf AG, 22339 Hamburg)
- Measuring cylinder (e.g. made of PP or PMP), 100 and 250 mL
- Volumetric flasks (PP), 10, 50, 100 and 250 mL
- Volumetric flask (PFA), 50 mL
- Disposable filter holder (PTFE membrane)
- Ultrapure water unit with reverse osmosis device and ultrapure water system for the production of ultrapure water ($\rho \geq 18.2$ MΩ × cm at 25 °C)
- Temperature and time programmable corrosion-proof dishwashing machine for alkaline and acidic rinse cycles, with ultrapure water the finishing rinse cycles

Abbreviations:
PTFE = polytetrafluoroethylene
PE = polyethylene
PP = polypropylene
PMP = polymethylpentene
PFA = perfluoroalkoxy polymer

Note
It is important to ensure that the plastics are cadmium-free when using disposable materials, the blank values of which must be checked.

1.2 Chemicals

- Nitric acid, 65%, < 0.5 ppb of Cd (the manufacturer must provide batch-dependent certification of content), e.g. Suprapur®, from Merck, 64293, Darmstadt, Germany
- Hydrochloric acid, 30%, < 0.5 ppb of Cd (the manufacturer must provide batch-dependent certification of content), e.g. Suprapur® from Merck
- Commercially available ICP-MS standard solution with a certified cadmium content of 1000 mg/L, traceable to a standard reference material, in diluted nitric acid, e.g. ICP multiple-element standard solution IV (Merck 111355)
- Commercially available ICP-MS standard solution with a certified cadmium content of 10 mg/L, traceable to a standard reference material, in diluted nitric acid, e.g. ICP multiple-element standard solution VI (Merck 110580)
- Tuning stock solutions according to the recommendation of the device manufacturer, e.g. Agilent 5184-3566 and 5188-6524
- Scandium standard solution of 1000 µg/mL, e.g. Plasma Standard Solution, Specpure®, from AlfaAesar
- Lutetium standard solution of 1000 µg/mL, e.g. Plasma Standard Solution, Specpure®, from AlfaAesar
- Ultrapure water, > 18 MΩ × cm at 25 °C
- Argon 5.0 (purity at least 99.999%)

1.3 Solutions

Hydrochloric acid, 25%:	204 mL of 30% hydrochloric acid (measured in the PP measuring cylinder) are placed into a 250 mL volumetric flask (PP) and then the volumetric flask is filled to the mark with ultrapure water.
Digestion mixture:	33.5 mL of 25% hydrochloric acid (measured in a PP measuring cylinder) are placed into a 100 mL volumetric flask (PP) and then the volumetric flask is filled to the mark with 65% nitric acid.
Tuning and rinsing solutions:	These solutions are prepared according to the recommendations of the device manufacturer. The following solutions are required for the measurement system Agilent 7500cx used in order to determine the characteristics of the method: Tuning solution 1: 50 µL of Agilent 5184-3566 tuning solution, 1 mL of 65% nitric acid and 250 µL of 30% hydrochloric acid are added into a 50 mL volumetric flask (PP), into which several mL of ultrapure water have been previously placed. The volumetric flask is then filled to the mark with ultrapure water.

	Tuning solution 2 (for the determination of the PA factor): 500 µL of each of the two Agilent 5188-6524 tuning solutions from the set are added into a 50 mL volumetric flask (PP), into which several mL of ultrapure water have been previously placed and acidified with 1.5 mL of 65% nitric acid. The volumetric flask is then filled to the mark with ultrapure water. Rinsing solution: 2.5 g of ethylenediaminetetraacetic acid (EDTA), 0.2 g of Triton X-100, 15 g of 25% ammonia solution and 20 g of 30% hydrogen peroxide are added into a 250 mL volumetric flask (PP) and then the volumetric flask is filled to the mark with ultrapure water. The solution is stored in the refrigerator and diluted by a factor of 10 immediately before use.
Internal standard:	Pipettes are used to add 200 µL of the scandium standard solution (1000 µg/mL), 10 µL of lutetium standard solution (1000 µg/mL) and 500 µL of 65% nitric acid into a 100 mL volumetric flask (PP). The volumetric flask is then filled to the mark with ultrapure water.
Calibration solution 1 mg/L:	Pipettes are used to add 50 µL of a commercially available ICP-MS standard solution (1000 mg/mL of Cd) and 500 µL of 65% nitric acid into a 50 mL volumetric flask (PFA). The volumetric flask is then filled to the mark with ultrapure water. The solution is stable for at least four weeks.
Control sample:	Pipettes are used to add 25 µL of a commercially available ICP-MS standard solution (10 mg/L of Cd), 500 µL of 65% nitric acid, as well as 500 µL of 25% hydrochloric acid into a 50 mL volumetric flask (PP). The volumetric flask is then filled to the mark with ultrapure water. The control solution must be freshly prepared every working day.

Calibration standards:

The calibration solutions shown in Table 1 are prepared on the basis of the prepared calibration solution (1 mg/L of Cd). The volumes of the calibration solutions listed in Table 1 are pipetted into 50 mL volumetric flasks (PP) and are acidified with 500 µL of 65% nitric acid as well as 500 µL of 25% hydrochloric acid in order to adjust the matrix. The volumetric flasks are then filled to the mark with ultrapure water.

Table 1 Calibration solutions

Solution	Pipetting volume [µL]	Concentration of cadmium in the solution [µg/L]	Concentration of cadmium in the air* (minimal dilution) [µg/m³]
Blank	0	0	–
Standard 1	25	0.5	0.03
Standard 2	250	5	0.3
Standard 3	2500	50	3

* for a digestion volume of 20 mL, an air sample volume of 1.2 m³ and a minimal dilution factor of 4

1.4 Storage stability of the solutions

The storage stability of elemental solutions, in particular the diluted elemental solutions, is limited. The information on storage stability provided by the manufacturer must be taken into consideration for commercially available starting solutions. Diluted elemental solutions must be freshly prepared at regular intervals (see Table 2).

Table 2 Storage stability of the elemental solutions

Cadmium concentration [µg/L]	Maximum storage duration in days
$100 \geq c > 0.1$	2
$1000 \geq c > 100$	14
$10\,000 \geq c > 1000$	30

2 Sampling

Sampling can be carried out as stationary or personal sampling. The caps of the filter transport capsules are removed for sampling and a nitrocellulose membrane filter (Ø 37 mm) is placed into the GSP or FSP sampling head (see Figure 1). Then a flow rate of 10 L/min is adjusted. At a sampling time of 2 hours this corresponds to an air sample volume of 1200 litres. After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discard the measurement (see DGUV Information 213-500 "General Part", Section 3 [2]). The relative humidity should be ≤ 50% [6].

In order to monitor the acceptance value, the filter batch used must be tested for its suitability before carrying out the measurements (see Section 4.2). In this case only filters from the tested batch may be used for sampling. The loaded filters are then removed from the sampling system and sealed with the caps of the transport capsules. The important parameters for determination of the concentration in air (sample volume, temperature, air pressure and relative humidity) are documented in the sampling record.

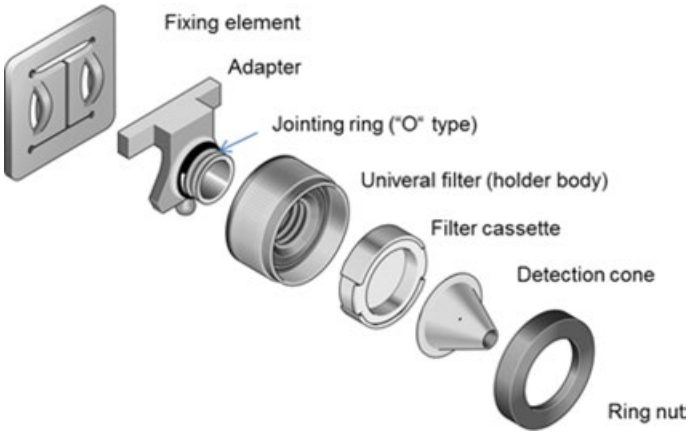

Figure 1 Schematic structure of the used PGP sampling system fitted with a GSP sampling head with a filter cassette [7]

3 Analytical determination

3.1 Sample preparation

The loaded filters are transferred into separate digestion cylinders made of quartz glass (see Figure 2) using a ceramic tweezer and a quartz/PTFE glass rod in each case. Then 10 mL of digestion mixture is added. After the air cooler has been attached, the vessels are heated in an aluminium heating block thermostat for 1.5 hours under reflux (block temperature approx. 130 °C). Then the heating block is removed from the thermostat. After the vessels have cooled to approx. 50 °C, 10 mL of ultrapure water are carefully added over each cooling tube for the purpose of rinsing the attached coolers and simultaneous primary dilution of the sample solution. The sample solutions are then heated for a further 30 minutes under reflux to ensure homogenisation.

After cooling and sedimentation, the vessels are sealed with PE caps and the volumes of the digestion solutions (sample solutions) are read off. In order to minimise resorption effects, the analytical determination is carried out immediately after sedimentation. In the case of stable suspensions partial volumes are filtered through disposable filters before analysis. The sample must be diluted with ultrapure water at a minimum ratio of 1 : 4 (v/v), in order to obtain a solution that is ready for measurement. For this purpose an aliquot of 2500 µL is pipetted into a 10 mL volumetric flask, which is then filled to the mark with ultrapure water.

In order to increase the probability of obtaining at least one measured value within the calibration range from each sample within a sequence it is advisable to pre-

Figure 2 Schematic illustration of a digestion vessel with attached cooler

pare additional diluted solutions (e.g. 1 : 40 and 1 : 400, pipetting volume of 250 or 25 µL to 10 mL) for measurement.

Blank value determination is carried out as described above, by subjecting non-loaded filters to the entire preparation method, whereby appropriate aliquots should also be prepared.

An autosampler transfers the prepared and diluted sample into the ICP-mass spectrometer and analysis is carried out using element isotopes as free from interference as possible.

3.2 Instrumental operating conditions

At least two blanks, as well as the calibration standards and the sample are analysed one after another in a sample sequence. A control sample must be analysed after 10 sample solutions of unknown concentration as well as at the end of each sample sequence. Before starting an analytical run, the ICP mass spectrometer must be tuned according to the manufacturer's instructions.

In order to check that measurement conditions remain stable, the internal standard solution is continuously added during the analysis. Alternatively, the internal standard solution can be added directly to the calibration and sample solutions. Elements that, on the one hand, are similar to the analyte in their mass and ionisation

potential and, on the other, are highly unlikely to be present in the sample should be selected as internal standards. This requirement must be checked in advance in the case of unknown samples, e.g. on the basis of the absolute intensities or through comparative calculations of several internal standards. Furthermore, their intensities should be in magnitudes that result in minimal signal scattering. At the same time, they should not themselves cause interference and undesired matrix effects.

The elements scandium (^{45}Sc) and lutetium (^{175}Lu) were selected for the measurement method described here, so that the method could be used for the simultaneous determination of a great number of other analytes. When specifying the internal standard for the evaluation the absence of these elements must be checked in all solutions. Alternatively, the second internal standard can be used after checking for its absence. Due to the considerable differences in the technical conception of the instrumental systems, it is not possible to provide generally valid detailed information on the instrumental parameters. The operating conditions, which were applied to determine the characteristics of the method, are summarised as an example below.

Operating conditions for the determination of the characteristics of the method:

Instrument:	Agilent 7500cx
Autosampler:	ASX-500
Sampler cone:	Ni
Skimmer cone:	Ni
Nebuliser:	Agilent MicroMist
Plasma torch:	Quartz 2.5 mm
Integration time:	0.5 s
Sampling period:	0.31 s
RF power:	1500 W
Sample depth:	8 mm
Carrier gas:	0.72 L/min
Make-up gas:	0.34 L/min
Extract 1:	0 V
Extract 2:	–130 V
Reaction gas:	–
Analyte isotope:	^{111}Cd
Internal standards:	^{45}Sc, ^{175}Lu
Flow rate (sample):	1.2 mL/min
Argon	18 L/min

When applying the stated parameters, the oxide formation rate was 0.76% and the proportion of double charges was 1.24%.

4 Evaluation

4.1 Calibration

The calibration function is linear over several decades under the selected operational conditions. The evaluation of the calibration points and blanks is carried out using the evaluation software supplied by the manufacturer, which generally yielded the solution concentrations of the samples directly in µg/L.

If the measured value is above the calibration range, then the sample solution is to be diluted appropriately and quantification has to be repeated using the dilute sample solution.

4.2 Monitoring of blank values

The limit of quantification of the method is significantly influenced by the scattering of the blank values in the collection phases used. If a large number of measurements are carried out over a longer period of time, it is necessary to check the batch-related blank values. In this case, it is advisable to determine at least one blank value in each sample sequence in the course of routine analysis.

The standard deviation is calculated using the ten remaining blank values taken from the twelve last measurements of blanks after eliminating the two measurements with the extreme values. According to DIN EN 13890 [3] the tenfold value of the standard deviation thus determined is taken as the basis of the limit of quantification of the method, if the batch of the collection phase was not checked.

Generally, the value for the limit of quantification of the method without checking the batch does not permit the assessment of compliance with the acceptance value for cadmium. The collection phases must originate from a consistent batch for the purpose of determination of the blanks and sampling for this investigation. Initially ten blank samples must be prepared and analysed from this batch according to DIN EN 13890 [3]. The tenfold value of the standard deviation of the analyte concentration in µg/L must then be compared with the solution concentration, which is equivalent to one fifth of the acceptance value at minimal dilution according to the sampling conditions described in Section 2. If the limit of quantification of the selected batch thus determined lies below the reference value of a fifth of the acceptance concentration, then this is suitable for limit value reference measurements with respect to the acceptance concentration (see TRGS 402, Annex 3, 3.1 (8) [5]).

4.3 Calculation of the analytical result

The cadmium concentration in the sample solution in µg/L is determined from the calibration function by means of the counting rate for the cadmium isotope with a mass/charge ratio of 111. The cadmium concentration c_L in the air sample in µg/m³ is obtained from Equation (1) as follows:

$$c_L = \frac{c_{LSG} * F * V_{LSG}}{1000 * V_{Air}} \quad (1)$$

If a significant and reproducible blank value has been found, then this must be taken into consideration in the calculation (see Equation (2)):

$$c_L = \frac{(c_{LSG} - c_{BW}) * F * V_{LSG}}{1000 * V_{Air}} \quad (2)$$

where:

c_B is the mean cadmium concentration of the diluted measuring solution of the prepared blank samples in µg/L
c_L is the mass concentration of cadmium in the air sample in µg/m³
c_{LSG} is the concentration of cadmium in the measuring solution in µg/L (obtained from the calibration curve)
F is a factor, which takes the dilution of the measuring solution into account (F = 4)
V_{LSG} is the read-off volume of the sample solution after digestion in mL
V_{Air} is the air sample volume in m³

4.4 Quality control

It is possible to control the stability of the physical measurement conditions by measuring the internal standards. The recoveries of both isotopes used (^{45}Sc and ^{175}Lu) should be between 95 and 105% during analysis of the sample.

The quality control is carried out using commercially available solutions (quality control standards) in the course of an analytical run. The aim is to check the accuracy of the calibration over the entire measurement duration. For this purpose, the control samples described in Section 1.3 are freshly prepared in each case and regularly measured. The deviation of the control samples from the nominal concentration (under the stated conditions 10 µg/L of Cd) must not exceed 5%.

5 Reliability of the method

5.1 Uncertainty

Estimation of the sampling-dependent components of the uncertainty is based on the following contributions according to Annex B of DIN EN 13890 [3]:

For sampling of inhalable dusts

Calibration of the test system:	0.5%
Estimation of the collected concentration:	4%
Systematic deviation from the sampling convention:	7.5%
Error contribution from sampling:	*8.5%*

For sampling of respirable dusts

Calibration of the test system:	1%
Estimation of the collected concentration:	1%
Systematic deviation from the sampling convention:	8%
Deviation from the nominal flow of the cyclone:	6%
Individual variability of the sampling device:	7%
Error contribution from sampling:	*12.3%*

Taking the sampling time of 120 minutes into account this results in a total error of 9.0% for the sampling of inhalable and 12.6% for the sampling of respirable dusts. If the upper limit for sample loss during transportation corresponds to the requirements of DIN EN 13205 [4], then a further uncertainty component of up to 2.9% associated with this loss must be included in the calculation.

Ten nitrocellulose membrane filters were each spiked with three solutions of different cadmium concentrations (40 µL each of Cd standard solution with 1, 25 and 100 mg/L) for the evaluation of the method and then they were subjected to the entire analytical procedure. The results are shown in Table 3.

Table 3 Variation coefficients for three different concentrations and 10 determinations in each case

Mass of Cadmium [µg]	Cadmium concentration [µg/L]*	Coefficient of variation [%]
0.04	0.5	2.8
1	12.5	1.3
4	50	0.7

* The concentrations result from digestion volumes of 20 mL and a dilution factor of 4

If all the listed error components are summarised, then the following values are obtained for the combined und the expanded uncertainty at a sampling time of two hours for inhalable and respirable dust with a flow rate of von 10 L/min (see Tables 4 and 5).

Table 4 Uncertainty for the determination of inhalable dust

Mass of Cadmium [µg]	Cadmium concentration [µg/L]	Cadmium concentration in air [µg/m³]	Combined uncertainty u [%]	Expanded uncertainty *U* [%]
0.04	0.5	0.033	9.9	19.7
1	12.5	0.83	9.5	19.1
4	50	3.3	9.5	19.0

Table 5 Uncertainty for the determination of respirable dust

Mass of Cadmium [µg]	Cadmium concentration [µg/L]	Cadmium concentration in air [µg/m³]	Combined uncertainty u [%]	Expanded uncertainty *U* [%]
0.04	0.5	0.033	13.2	26.5
1	12.5	0.83	13.0	26.0
4	50	3.3	12.9	25.9

5.2 Limit of quantification

The limit of quantification of the basic analytical method was determined from an equidistant 10-point calibration in the concentration range of 0.1 to 1 µg/L of Cd as stipulated in DIN 32645 [8]. The absolute limit of quantification is 0.11 µg/L. This is equivalent to a relative limit of quantification of 0.007 µg/m³ for an air sample volume of 1.2 m³, a digestion volume of 20 mL and a minimal sample dilution of 1 : 4.

However, this only applies when using a homogeneous sample carrier batch with a controlled low and only slightly scattered blank value, which can be considered negligible in this case. According to DIN EN 13890 [3] an absolute limit of quantification of 6 µg/L is obtained from the scatter of the long-term blank for sample carrier batches that have not been checked and a relative limit of quantification of 0.5 µg/m³ (air sample volume of 1.2 m³, digestion volume of 20 mL, dilution factor of 4).

The limit of quantification can be further lowered at workplaces with only a small amount of airborne dust by increasing the sampling time. The sampling time should, however, only exceed four hours in exceptional cases.

5.3 Linearity

Taking the blank into account, an equidistant 10-point calibration in the range of 0 to 90 µg/L showed that there was no significantly better fit using a non-linear calibration function at a correlation coefficient of r = 0.9999 according to Mandel's fitting test.

5.4 Selectivity

High concentrations of other elements and compounds can lead to interference. In the case of the principally unknown samples the measurement results must be checked for possible interference and, if necessary, a suitable dilution step must be selected in order to achieve a valid result. Non-spectral interference and matrix effects can be reduced by means of a suitable dilution.

A multitude of polyatomic interferences can be minimised by the use of different cell technologies.

Isobaric interferences should be avoided by selection of alternative isotopes if possible. If no alternative isotopes are available and the use of a cell technology does not lead to a sufficient reduction of the interferences, then robust plasma conditions should be selected to enable an arithmetically derived interference correction. An isotope with the mass of 111, which makes up 12.8% of the naturally occurring metal, is used for the cadmium determination by means of ICP mass spectrometry. Polyatomic interferences, that have the same mass/charge ratio as the ^{111}Cd isotope, can be caused by the cations $^{95}Mo^{16}O^+$ and $^{39}K_2{}^{16}O_2{}^1H^+$, for example.

A cadmium analysis of basically unknown samples on the basis of ICP mass spectrometry without reaction technology is futile. False positive results cannot be excluded, as the cadmium isotopes experience severe interference from molybdenum oxide ions. The use of oxygen as a reactant has proved successful in minimising interference in such cases. The collision modes of the various manufacturers of spectrometers do not lead to sufficiently reliable results in the presence of interfering thermodynamically stable metal oxides.

Matrix problems in unknown samples as well as temporary changes in the properties of the cones can be observed due to the use of an internal standard. As a result of unknown sample matrices and stress on the system from analyte concentrations of an unknown high level, the purge time should be as long as possible after each measurement and the cones should be replaced regularly.

Under certain circumstances, further suitable dilution steps must be carried out in order to obtain a valid result.

5.5 Recovery

As a result of the different chemical composition and the different physical properties of the aerosols in the air 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 13890 [3] (restricted to those metals and compounds that are soluble in the stated system) [3, 5].

The conversion rate of the digestion procedure of the poorly soluble compounds cadmium sulphide and cadmium oxide were checked as an example following the recommendations provided in DIN EN 13890 [3]. For this purpose six filters were each spiked with both of the compounds (weighing approx. 10 mg, tolerance of ± 0.01 mg) and subjected to the entire analysis process. The mean recovery was determined as 102.0% for both cadmium sulphide and cadmium oxide.

5.6 Storage stability

It can be assumed that cadmium and its inorganic compounds are stable with regard to the mass concentration of the elements on the sample carrier. Possible losses during storage occurring between sampling and analysis can therefore be neglected.

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