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Expert Committee Chemistry

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Method for the determination of cadmium

Method tested and recommended by the Berufsgenossenschaften for the determination of cadmium and cadmium compounds in working areas after discontinuous sampling.
For the assessment of working areas, both personal or stationary sampling are possible:

1 Sampling with a pump and collection on a particle filter,
atomic absorption spectrometry with flame technique and graphite furnace technique after acid digestion.
“Cadmium-1-AAS”
(Issue: November 1994)

For the determination of cadmium chloride cf. also method ZH 1/120.14.

IUPAC name:	**CAS No:**
Cadmium	7440-43-9

1 Sampling with a pump and collection on a particle filter, atomic absorption spectrometry with flame technique and graphite furnace technique after acid digestion

This method permits the determination of the concentrations of cadmium and cadmium compounds in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a filter. After acid digestion, the cadmium in the deposited aerosol is determined by atomic absorption spectrometry (AAS).

Technical data:

Table 1. Relative quantification limit with cellulose ester membrane filters.

Sample volume m^3	Extraction volume mL	Filter diameter cm	Quantification limit in the air sample µg/m^3	Lowest detectable concentration (measuring solution) µg/L	Method
0.42[1)]	20	3.7	0.10	2.1	GFAAS[3)]
45[2)]	75	15	0.17	100	FAAS[4)]

[1)] Personal sampling, e.g. sampling system carried by a person (PSS) according to the Institute for Occupational Safety (BIA), equipped with suitable pump [1]

[2)] Stationary sampling, e.g. VC 25 G [2, 3]

[3)] GFAAS: Graphite furnace AAS

[4)] FAAS: Flame AAS

Selectivity: Selective measurements are possible with both techniques. The selectivity must, however, be checked in each individual case. Interference may arise especially in the presence of high silicon (AAS flame technique) and high chlorine concentrations (AAS graphite furnace technique).

Advantages: The graphite furnace technique is a very sensitive method.

Disadvantages: Very time-consuming, sophisticated equipment needed.

Apparatus: Sampling device consisting of a sampling head with particle filter, pump equipped with gas meter or flow meter and timer, atomic absorption spectrometer with background compensation, equipment for the flame technique, graphite furnace with closed-circuit cooling and autosampler.

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

All chemicals, solutions and vessels must have been checked for cadmium blank values and their mean variations. The results may lead to an increase of the quantification limit (cf. Sect. 6.3 “Blank value”).

1.1 Equipment

For sampling:

Samplers for the collection of aerosols are suitable with a sampling characteristic in accordance with the recommendations [1–3, 14, 15] (e.g. PSS according to the Institute for Occupational Safety (BIA) from GSM GmbH, Neuss-Nerf) equipped with an appropriate pump. The flow rate of the pumps used must be sufficiently independent of the pressure drop at the filter (e. g. Du Pont Alpha 1 from DEHA-Haan & Wittmer GmbH, Friolzheim; GSA 5002 Ex from GSA Co., Neuss; Gillian PP5, Du Pont 4000 AA and VC 25 G from GSM GmbH, Neuss-Nerf)

Cellulose ester membrane filters, pore size 0.8–1.2 µm (e.g. from Sartorius, Göttingen; Nuclepore, Tübingen). With the test aerosol, paraffin oil mist, the permeability of the filters must not exceed 0.5% [4–6]

For sample preparation and analytical determination:

Aluminium heating-block thermostat with bore holes for digestion vessels

Graduated glass digestion cylinders (accuracy class A or B) with internal ground joint, bumping sticks (e. g. glass rod with a piece of polytetrafluoroethylene (PTFE) tubing over the tip) and air condensers (length about 40 cm). The blank value must be checked separately before each use

Ceramic forceps

Disposable filters (PTFE membrane) in holders:

for filters of 3.7 cm diameter: 25 mL digestion cylinder, 0.2 mL graduation, NS 19/26 for filters of 15 cm diameter: 100 mL digestion cylinder, 1 mL graduation, NS 29/32

50 mL, 100 mL PTFE or polypropylene volumetric flasks for standard and calibration solutions

Atomic absorption spectrometer with background compensator, equipment for the flame technique and the graphite furnace technique, autosampler for the graphite furnace technique/graphite tubes equipped with platform/cadmium hollow-cathode lamp/computer for control, registration and calibration, for the graphite furnace techniques with signal display via a monitor/printer

1.2 Chemicals

The following chemicals are needed for acid digestion of loaded filters and for the subsequent determination:

Hydrochloric acid, 25 %, analytical grade (e. g. Merck, Darmstadt)

Nitric acid, > 65 %, analytical grade (e. g. Merck, Darmstadt)

Ultrapure water, electrical conductivity $\leq 6\ \mu S \cdot m^{-1}$ at 25 °C

Gases:

Flame technique: Air/acetylene (welding quality)

Graphite furnace technique: Argon 4.6 (purity 99.996)

1.3 Solutions

Digestion mixture:

2 Parts by volume of nitric acid and 1 part by volume of hydrochloric acid.

Diluted digestion mixture:

1 Part by volume of ultrapure water and 1 part by volume of digestion mixture.

Standard solutions:
Cf. Tab. 2

Table 2. Standard solutions.

No	Term	Cd concentration	Matrix	Cation number	Manufacturer
1	Cadmium ICP-standard solution	1000 mg/L	Nitric acid (0.8 mol/L)	1	Johnson Mathhey Alfa Products, Karlsruhe
2	ICP multi element standard solution I	20 mg/kg ≙ 20.6 mg/L	Nitric acid (1 mol/L)	19	Merck, Darmstadt

Cadmium calibration solutions:
The cadmium calibration solutions were prepared by taking known volumes from the cadmium standard solutions and diluting them in 100 mL and 50 mL volumetric flasks with the diluted digestion mixture according to Tabs. 3 and 4.

Table 3. Cadmium calibration solutions No 1–5.

Calibration solution No	Prepared from standard solution No	Prepared from Calibration solution No	Concentration mg/L	Aliquot volume mL	Final volume mL	Final concentration mg/L
1	1	–	1000	1	100	10.0
2	2	–	20.6	5	50	2.06
3	–	1	10.00	5	50	1.00
4	–	2	2.06	5	50	0.21
5	–	3	1.00	5	50	0.10

Table 4. Cadmium calibration solutions No 6–11.

Calibration solution No	Prepared from standard solution No	Prepared from Calibration solution No	Concentration mg/L	Aliquot volume mL	Final volume mL	Final concentration µg/L
6	–	5	100	1.5	100	1.50
7	–	5	100	1	100	1.00
8	–	6	1.50	25	50	0.75
9		7	1.00	25	50	0.50
10	–	4	210	1	100	2.10
11	–	10	2.10	5	50	0.21

Matrix modifier for the graphite furnace technique:
Ammonium dihydrogen phosphate, w ($NH_4H_2PO_4$) = 20 g/L, prepared from “Suprapur” solutions from Merck, Darmstadt [7, 8, 10, 11].

2 Sampling

With a pump a measured air volume is drawn through a particle filter placed in a special sampling head (cf. Sect. 1.1): stationary sampling, e.g. VC 25 G, air flow rate 22.5 m^3/h with sampling for 2 hours, personal sampling, e.g. PSS with Du Pont P 4000 AA, air flow rate 210 L/h with sampling for 2 hours.

If there is a risk of overloading the filter because the aerosol concentrations are too high, it is recommended according to TRGS 402/3.4 that you reduce the sampling time and increase the sample numbers [9].

3 Analytical determination

3.1 Sample preparation

With the ceramic forceps and a bumping stick the loaded filter is transferred to the digestion cylinder. The digestion mixture is then added.

The 3.7 cm filters are overlaid with 10 mL of the digestion mixture and the 15 cm filters with 40 mL. Air condensers are connected to the digestion cylinders (25 mL and 100 mL). In an aluminium block thermostat they are kept under reflux for two hours (about 125 °C block temperature). Then 10 mL (35 mL) distilled water is carefully added through the reflux condenser. After cooling and sedimentation, the volume of the digestion solution (sample solution) is noted. To minimize absorption effects the atomic absorption spectrometric determination is carried out immediately after sedimentation. If the suspensions are stable partial volumes are filtered prior to the analytical determination.

Unloaded filters are analysed in the same way to determine the blank value.

3.2 Instrumental operating conditions

The method was characterized under the following instrumental conditions:

Apparatus:	Perkin Elmer, Überlingen AAS PE 5000 with deuterium background compensator (for the flame technique), AAS PE 1100 B with deuterium background compensator (for the graphite furnace technique), Autosampler AS-70, Graphite furnace HGA 700.

First the sample solution is analysed using the flame technique. A new determination using the graphite furnace technique is necessary if the flame technique yields results below the quantification limit.

3.2.1 Flame technique

Acetylene/air flame, oxidizing mode, evaluation according to the calibration curve procedure.

Table 5. Instrumental operating conditions for the flame technique.

Measuring range µg/L	Wavelength nm	Spectral slit width nm	Lamp current mA
100–2060	228.8	0.7	4

Higher concentrations are determined after appropriate dilution steps (to be taken into account in the calculation in Sect. 4.2).

3.2.2 Graphite furnace technique

Inert gas: argon, determination with matrix modifier (cf. Sect. 1.3) and evaluation according to the standard addition method.

Table 6. Instrumental operating conditions for the graphite furnance technique.

Measuring range µg/L	Wavelength nm	Spectral slit width nm	Lamp current mA
0.21–1.50	228.8	0.7	3

Pre-dilution of the sample solution 1:10 (cf. Sect. 5.3). Higher concentrations are determined after appropriate further dilution (to be taken into account in the calculation in Sect. 4.2).

The following sample solutions are prepared from the diluted sample solution and the calibration solution according to Tab. 7.

Table 7. Pipetting schedule for the standard addition method.

Measuring solution No	Volume of the sample solution diluted 1:10 µL	Volume calibration solution from Tab. 4 µL	Volume of the ultra pure water µL	Concentration of the calibration solution from Tab. 4 µg/L
0	0	0	1000	0.00
1	500	0	500	0.00
2	500	500 (No 6)	0	1.50 (No 6)
3	500	500 (No 8)	0	0.75 (No 8)
4	500	500 (No 11)	0	0.21 (No 11)

First of all 10 µL of the matrix modifier are pipetted into the graphite furnace and dried using programme steps one and two of the temperature/time programme shown in Tab. 8. Then 20 µL of the sample solution is added, and steps 3–9 are carried out to analyse the solution.

Table 8. Temperature/time program.

Programme step:	1	2	3	4	5	6	7	8	9
Furnace temperature in °C	90	130	90	130	350	500	500	1900	2650
Heating time in s	–	10	–	10	10	10	1	0	1
Hold time in s	–	20	–	20	20	10	5	5	5
Int. Argon flow rate in mL/min	3	300	300	300	300	300	40	40	300

1 Pipetting/matrix modifier
2 Drying
3 Pipetting/measuring solution
4 Drying
5, 6, 7 Thermal pretreatment
8 Atomization/measurement
9 Heating

4 Evaluation

4.1 Calibration

Calibration of the atomic absorption spectrometer can be carried out by different methods. The calibration curve method is suitable for the flame technique. The absorbances obtained with the sample solution are directly compared with the absorbances from the calibration curve.

The standard addition method is recommended for the graphite furnace technique. Calibration is carried out with solutions obtained by adding gradually increasing concentrations to the aliquots of the 1:10 diluted sample solution. The evaluation is made by extrapolation of the reference function to an absorbance of zero. Determination of the reference function and the measured value is carried out with a built-in computer. The calculations are based on the signal response areas.

4.2 Calculation of the analytical result

The cadmium concentration by weight in the air sample in µg/m^3 is calculated according to the equations (1) and (2):

$$w = (c_1 \cdot V_1) - w_1 \qquad (1)$$

$$c_w = \frac{w}{V} \qquad (2)$$

Legend:

w Cadmium weight of the sample solution in µg corrected for the blank value
c_1 Cadmium concentration of the sample solution in µg/L
V_1 Volume of the sample solution in L
w_1 Blank value in µg calculated as cadmium
c_w Cadmium concentration by weight in the air sample in µg/m^3
V Air sample volume in m^3

5 Reliability of the method

5.1 Accuracy

At three different concentrations and $n = 8$ determinations the following data were obtained:

Table 9. Standard deviation (rel.) *s*.

Method	Measuring range µg/L	Concentration of the calibration solution µg/L	Standard deviation (rel.) *s* %
FAAS	100–2060	210	4.9
		1000	2.8
		2060	2.0
GFAAS	0.21–1.50	0.50	6.8
		0.75	4.5
		1.00	3.4

5.2 Quantification limit

The relative quantification limits were determined as ten times the mean variation of the blank values obtained with the cellulose ester membrane filters, reagents and vessels used (8 filters from each of two batches).

Table 10. Quantification limit.

	GFAAS	FAAS
Filter diameter in cm	3.7	15
Air sample volume in m^3	0.42 [1]	45 [2]
Volume of the sample solution in mL	20	75
Quantification limit in the sample solution in µg/L	2.1 [3]	100
Quantification limit in the air sample in µg/m^3	0.10	0.17

[1] For personal sampling (e.g. with PSS and a suitable pump)

[2] For stationary sampling (e. g. VC 25 G)

[3] For the 1:10 diluted sample solution the quantification limit was 0.21 µg/L (cf. Sect. 5.3)

5.3 Selectivity

Both techniques allow selective measurements.
However, the selectivity must be checked in each individual case. Interferences may arise especially with high silicon concentrations. High hydrochloric acid concentrations interfere in the graphite furnace technique, presumably because of the formation of volatile cadmium chloride compounds. For this reason pre-dilution of the samples and careful determination of the maximum temperature of the thermal pretreatment are necessary. The presence of arsenic may lead to spectral interference.

5.4 Recovery

Due to the different chemical composition and the different physical properties of the aerosols in various working areas a generally valid statement about the recovery of the complete method cannot be made.

It is possible to make a statement for sample preparation and measurement. The cellulose ester membrane filters are loaded with measured volumes of the calibration solutions, digested and analysed.

The values listed in Table 11 were obtained from $n = 8$ determinations:

Table 11. Recovery rate.

Method	Filter diameter cm	Loaded cadmium weight µg	Recovery %
FAAS	15	75	102
GFAAS	3.7	0.015	96

6 Discussion

6.1 Graphite furnace technique

The matrix modifier ammonium dihydrogen phosphate causes conversion of highly volatile cadmium compounds into the non-volatile phosphate and consequently permits higher pretreatment and atomization temperatures. The ammonium ions and the nitric acid help to remove the interfering chloride as volatile components (ammonium chloride or hydrochloric acid) in the thermal pretreatment.

Generally the excess phosphate leads to a background signal which cannot be sufficiently corrected by the deuterium background correction if the measuring signal and the background signal appear simultaneously. Sufficient compensation of this interference can be achieved by the use of graphite furnaces equipped with a platform, a heating rate above 2000 °C per second and an atomization temperature of 1900 °C. A programme check which is independent of the instrument is required. Zeeman background correction is recommended for an additional decrease in this interference [12].

6.2 Digestion methods

The digestion conditions described in Sect. 3.1 are selected to ensure the detection of airborne cadmium and the cadmium compounds usually found at workplaces. The preparation is therefore suitable for most of the industrially used cadmium compounds, e. g. cadmium (metal), cadmium chloride, cadmium iodide, cadmium nitrate, cadmium oxide, cadmium sulfide, cadmium stearate and cadmium sulfate [13].

In doubtful cases, solubility tests must be carried out with the materials used in the working areas [12].

6.3 Blank value

Among other things the quantification limit is dependent on the mean variation of the blank values obtained with the filter materials.

If other materials are to be used, e. g. deep filters of glass fibre or quartz fibre the following restrictions must be observed:

If glass fibre filters are used acid-soluble constituents can lead to great fluctuations in the blank values and to interference (e.g. due to a high level of soluble silicates). Glass and quartz fibre filters can cause interference resulting from absorption effects during the digestion, especially at low cadmium concentrations. These effects must also be considered with some batches of membrane filters made of cellulose ester, mainly as a result of the different natural or anthropogenic heavy metal content of the cellulose raw material.

The cadmium blank value (cf. Sect. 3.1) is understood here as the mean value of the measurements of several cellulose ester membrane filters from different batches. They are individually prepared and analytically determined so that the blank values and mean variations reflect the filter materials, the reagents and the vessels used.

7 References

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