Carcinogenic metals – Determination of arsenic, beryllium, cadmium, cobalt, nickel and their particulate compounds in workplace air using inductively coupled plasma mass spectrometry (ICP-MS)

Air Monitoring Method

K. Pitzke[1]

T. H. Brock[2,*]

R. Hebisch[3,*]

A. Hartwig[4,*]

MAK Commission[5,*]

1 Method development, Institute for Occupational Safety and Health of the DGUV (IFA), German Social Accident Insurance (DGUV), Alte Heerstraße 111, 53757 Sankt Augustin, Germany

2 Head of the working group "Analytics", German Social Accident Insurance, Institution for the raw materials and chemical industry, Prevention – Department of Hazardous Substances, Biological Agents and Analytical Chemistry, Kurfürsten-Anlage 62, 69115 Heidelberg, Germany

3 Head of the working group "Air Analyses" of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany

4 Chair of the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Institute of Applied Biosciences, Department of Food Chemistry and Toxicology, Karlsruhe Institute of Technology (KIT), Adenauerring 20a, Building 50.41, 76131 Karlsruhe, Germany

5 Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn, Germany

* email: T. H. Brock (analytik@bgrci.de), R. Hebisch (luftanalysen-dfg@baua.bund.de), A. Hartwig (andrea. hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)

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Please direct correspondence to Berufsgenossenschaft Rohstoffe und chemische Industrie, Prävention, P.O. Box 101480, 69004 Heidelberg, Germany; analytik@bgrci.de

Abstract

This analytical method is a validated measurement procedure for the determination of arsenic [7440-38-2], beryllium [7440-41-7], cadmium [7440-43-9], cobalt [7440-48-4], nickel [7440-02-0] and their particulate compounds after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a nitrocellulose membrane filter using a suitable flow-regulated pump. After acid digestion, the elements retained on the filter are analysed using inductively coupled plasma mass spectrometry. The relative limits of quantification are between 0.00029 μg/m^3 for beryllium and 0.11 μg/m^3 for nickel for an air sample volume of 1.2 m^3. The mean recovery was between 97% for arsenic and 111% for beryllium. The concentration-dependent

expanded uncertainty was 21% to 28%. This analytical method has been accredited by the accident insurance companies for the detection in workplace air of substances that are carcinogenic, mutagenic or toxic to reproduction. This method has been tested and recommended for the determination of arsenic in work areas by the German Social Accident Insurance (DGUV). Both personal and stationary sampling can be performed for measurements in order to evaluate work areas.

Name	CAS No.	Molar mass [g/mol]	Formula	Assessment criteria [µg/m³][a]
Arsenic compounds, classified as Carc. 1A, Carc. 1B	7440-38-2	74.92	As	TC 8.3 (I) EF 8 (AGS 2023 a) AC 0.83 (I) (AGS 2023 a)
Beryllium and beryllium compounds	7440-41-7	9.01	Be	OELV 0.14 (I) EF 1 (I), 0.06 (R) EF 1 (I) (AGS 2023 c)
Cadmium and cadmium compounds, classified as Carc. 1A, Carc. 1B	7440-43-9	112.41	Cd	TC 2.0 (R) EF 8 (AGS 2023 a) AC 0.9 (R) (AGS 2023 a)
Cadmium and inorganic cadmium compounds	7440-43-9	112.41	Cd	OELV 2.0 (I) EF 8 (AGS 2023 c)
Cobalt and cobalt compounds, classified as Carc. 1A, Carc. 1B	7440-48-4	58.93	Co	TC 5.0 (R) EF 8 (AGS 2023 a) AC 0.5 (R) (AGS 2023 a)
Nickel compounds, classified as Carc. 1A, Carc. 1B	7440-02-0	58.69	Ni	TC 6.0 (R) EF 8 (AGS 2023 a) AC 6.0 (R) (AGS 2023 a)
Nickel and nickel compounds	7440-02-0	58.69	Ni	OELV 30 (I) EF 8 (II) (AGS 2023 c)
Metallic nickel	7440-02-0	58.69	Ni	OELV 6.0 (R) EF 8 (II) (AGS 2023 c)

AC: acceptable concentration; EF: excursion factor, short-term value category in parentheses; I: inhalable fraction; OELV: occupational exposure limit value; R: respirable fraction; TC: tolerable concentration
[a] The concentrations refer to the metal content of the respective compound.

The method was validated for cadmium and cadmium compounds based on the assessment criteria valid until 2020 with an acceptable concentration (AC) of 0.16 µg/m³ (R) and a tolerable concentration (TC) of 1.0 µg/m³ (I). The method is also suitable based on the assessment criteria valid since 2021 (see above).

The exposure-risk relationship that was derived for nickel compounds is valid for all nickel compounds classified as Category 1A or 1B carcinogens. An occupational exposure limit value (OELV) of 6 µg/m³ (R) was established for activities involving exposure to metallic nickel (carcinogenic, Category 2) according to TRGS 900 (AGS 2023 c). The OELV of metallic nickel can be used for the evaluation if a sample contains only metallic nickel. If dusts that contain nickel are generated during work activities, and these are assumed to undergo only surface oxidation, the evaluation is performed using the same procedure as for mixtures containing metallic nickel. In general, when thermal processes are carried out in the presence of atmospheric oxygen, this will lead to the formation of oxidic nickel compounds.

The OELV for the inhalable fraction of nickel was not taken into consideration at the time of validation. However, the method is suitable for monitoring purposes and has proven effective in practice.

The method is likewise suitable for monitoring short-term values for arsenic, cadmium, cobalt and nickel over a sampling period of 15 minutes.

1   Summary

This method involves the use of personal or stationary sampling procedures to determine the mean concentrations of carcinogenic metals (arsenic, beryllium, cadmium cobalt, nickel) and their particulate compounds in the work area over the sampling period.

Measurement principle: A pump is used to draw a defined volume of air through a membrane filter. After acid digestion, the fraction deposited on the filter is analysed by inductively coupled plasma mass spectrometry (ICP-MS) for metals classified as carcinogenic (arsenic, beryllium, cadmium, cobalt and nickel).

Limits of quantification:

Absolute:

Arsenic	0.0017 µg per sample carrier
Beryllium	0.00035 µg per sample carrier
Cadmium	0.013 µg per sample carrier
Cobalt	0.035 µg per sample carrier
Nickel	0.13 µg per sample carrier

Relative:

Arsenic	0.0014 µg/m^3
Beryllium	0.00029 µg/m^3
Cadmium	0.011 µg/m^3
Cobalt	0.029 µg/m^3
Nickel	0.11 µg/m^3

Sampling for 2 h at 10 l/min, 20 ml of sample solution, dilution factor of 10

Measurement range:

Range of the analytical procedure:

Arsenic	0.1–100 µg/l
Beryllium	0.01–1 µg/l
Cadmium	0.01–10 µg/l
Cobalt	0.01–10 µg/l
Nickel	0.05–10 µg/l

Validated measurement range:

Arsenic	0.0014–16.6 µg/m^3
Beryllium	0.00029–0.12 µg/m^3
Cadmium	0.011–2.0 µg/m^3
Cobalt	0.029–10 µg/m^3
Nickel	0.11–12 µg/m^3

based on an air sample volume of 1.2 m^3

Selectivity: The selectivity of the method depends above all on the choice of isotope, the absence of spectral interference and the minimisation of non-spectral interference.

Advantages: Measurements with high sensitivity can be taken by personal sampling; short-term measurements are possible.

Disadvantages: Does not detect concentration peaks; requires sophisticated equipment and is time consuming.

Apparatus: Sampling devices:
Pump and sampling head, filter holder with membrane filter and supporting sieve
Volumetric flow meter
digestion apparatus
inductively coupled plasma mass spectrometer (ICP-MS) and reaction cell (e.g. collision mode).

2   Equipment and chemicals

The materials, consumable products and chemicals listed in this section were used to determine the characteristics of the method described below. Substitutions may be made if they are of the same quality and purity, e.g. perfluoroalkoxy copolymer (PFA) instead of quartz glass. Consumable products and chemicals, etc., have to be checked for blank values and sources of interference before use. These must be taken account of if present.

2.1   Equipment

For sampling:

- Pump for personal sampling and stationary sampling with a nominal flow rate of 10 l/min (e.g. SG10-2, from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- GSP10 sampling head (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- FSP10 sampling head with cyclone separator (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- PGP filter cassette made of plastic, supplied with covers for the filters with a diameter of 37 mm (e.g. from GSA Messgerätebau GmbH, 40880 Ratingen, Germany)
- Supporting sieve, 37 mm (e.g. from Metaq GmbH, 42115 Wuppertal, Germany)
- Membrane filter, diameter 37 mm, pore size 8.0 µm, cellulose nitrate, preferably certified for metal content (e.g. from Sartorius AG, 37075 Göttingen, Germany)
- Volumetric flow meter (e.g. from TSI GmbH, 52068 Aachen, Germany)

For the sample preparation:

- Heating block thermostat made of metal or graphite with time and temperature control, operating range up to 200 ℃ (e.g. from Gebr. Liebisch GmbH & Co., 33649 Bielefeld, Germany)
- Graduated digestion vessels with air cooler made of quartz glass (diameter 19 mm, maximum volume 25 ml) with ground-glass joints (ST 19/26), acid-proof 0.2-ml graduations from 15 to 25 ml (e.g. from VWR International GmbH, 64295 Darmstadt, Germany)
- Graduated digestion vessels with air cooler made of quartz glass (diameter 28 mm, maximum volume 100 ml) with ground-glass joints (ST 29/32), acid-proof 0.5-ml graduations from 75 to 100 ml (e.g. from VWR International GmbH, 64295 Darmstadt, Germany)
- Glass rods (diameter about 4 mm) made of quartz glass fitted with replaceable endpieces of polytetrafluoroethylene (PTFE) tube (e.g. from VWR International GmbH, 64295 Darmstadt, Germany); standard glass rods cannot be cleaned without leaving a residue
- Polyethylene stoppers for the digestion vessels (ST 19/26) (e.g. from Pöppelmann GmbH & Co. KG, 49378 Lohne, Germany)
- 5-litre bottle made of PFA with PTFE dispenser for rinsing the air cooler and preparing dilutions (e.g. Optifix HF dispenser, 30 ml, from Poulten & Graf (Fortuna), 97877 Wertheim, Germany)
- Measuring cylinders made of PFA, 500 ml, 100 ml, 50 ml (e.g. from VITLAB GmbH, 63762 Großostheim, Germany)
- 2.5-litre quartz bottle with lateral filler neck (ST 29/32), sealable with air-permeable PTFE ground-glass stopper and PTFE ("hydrofluoric acid") dispenser as a bottle attachment, custom-made (e.g. from VWR International GmbH, 64295 Darmstadt, Germany); for dispensing of freshly prepared standard acid mixtures into the digestion vessels
- Ceramic tweezers for transferring the membrane filters to the digestion vessels (e.g. from PLANO GmbH, 35578 Wetzlar, Germany)

For the analytical determination:

- Quadrupole ICP mass spectrometer with a collision/reaction cell and autosampler, concentric quartz nebuliser with cooled Scott double-pass spray chamber made of quartz glass
- Volumetric flasks made of PFA for standard and calibration solutions with screw caps and ring mark, 10 ml, 50 ml, 100 ml, 500 ml (e.g. from VITLAB GmbH, 63762 Großostheim, Germany)
- Vessels for standard/calibration solutions and sample vials for ICP-MS: polypropylene vessels (PP vessels) with screw caps (tested for blank values), graduated, 0.5 ml increments, maximum volume 15 ml, for autosamplers (e.g. from Greiner Bio-One GmbH, 72636 Frickenhausen, Germany)
- Positive displacement dispenser system for precise and automated sequential dosing of internal standard and for bringing to volume with dilution solution (see Section 2.3)
- Various adjustable piston pipettes to cover a volume range of 2 µl to 10 ml, air displacement: for aqueous solutions and suspensions with a density and viscosity similar to water (e.g. Socorex Acura 825 (2 to 1000 µl), Socorex Acura 835 (500 to 5000 µl and 1000 to 10000 µl), Socorex Isba S.A., Ecublens, Switzerland)
- Electronic precision balance
- Ultrapure water system with reverse osmosis unit and water purification system for the preparation of ultrapure water (specific resistance $\rho \geq 18.2$ M$\Omega \times$ cm at 25 ℃), reduction of the overall metal content, in particular for the production of water that is low in boron and alkalis (e.g. GenPure with X-CAD, from Wilhelm Werner GmbH, 51381 Leverkusen, Germany)

2.2 Chemicals

- Ultrapure water (specific resistance $\rho \geq 18.2$ M$\Omega \times$ cm at 25 ℃)
- Nitric acid, 65%, low metal content, batch certification by the manufacturer (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Hydrochloric acid, 30%, low metal content, batch certification by the manufacturer (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Nitric acid, 67–70%, low metal content, batch certification by the manufacturer (e.g. INSTRA-ANALYZED Plus for the trace analysis of metals, J.T. Baker, from Fisher Scientific GmbH, 58239 Schwerte, Germany)
- Scandium standard for ICP, 1000 mg/l, Sc_2O_3 in 7% HNO_3 (e.g. CertiPUR, traceable to NIST SRMs, from Merck KGaA, 64293 Darmstadt, Germany Order No. 170349)
- Tellurium standard for ICP, 1000 mg/l, Te in 5% HNO_3 (e.g. Specpure, traceable to NIST SRMs, Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 44632)
- Yttrium standard for ICP, 1000 mg/l, Y_2O_3 in 5% HNO_3 (e.g. Specpure, traceable to NIST SRMs, Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 13855)
- Lutetium standard for ICP, 1000 mg/l, Lu_2O_3 in 2–3% HNO_3, (e.g. Certipur, traceable to NIST SRMs, from Merck KGaA, 64293 Darmstadt, Germany Order No. 170330)
- Arsenic standard for ICP, 1000 mg/l, As in 5% HNO_3 (e.g. Specpure, traceable to NIST SRMs®, Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 13836)
- Cobalt standard for ICP, 1000 mg/l, Co in 2% HNO_3, (e.g. traceable to NIST SRMs, from PerkinElmer LAS, 63110 Rodgau, Germany, Order No. N9303735)
- Nickel standard for ICP, 1000 mg/l, Ni in 2% HNO_3 (e.g. traceable to NIST SRMs, from PerkinElmer LAS, 63110 Rodgau, Germany, Order No. N9300177)
- Cadmium standard for ICP, 1000 mg/l, Cd in 5% HNO_3 (e.g. Specpure, traceable to NIST SRMs, Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 13813)

- Beryllium standard for ICP, 10 mg/l, $Be_4O(C_2H_3O_2)_6$ in 2% HNO_3 (e.g. Specpure, traceable to NIST SRMs, Alfa Aesar, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 45248)

- Nickel powder, spherical, 400 mesh, purity 99.8% (metals basis) (e.g. Alfa Aesar, traceable to NIST SRMs, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 43704)

- Beryllium oxide, purity 99.95% (metals basis) (e.g. Alfa Aesar, traceable to NIST SRMs, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 35480)

- Cobalt powder, 400 mesh, purity 99.5% (metals basis) (e.g. Alfa Aesar, traceable to NIST SRMs, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 44085)

- Arsenic trioxide, purity ≥ 99.99% (metals basis) (e.g. Alfa Aesar traceable to NIST SRMs, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 40370)

- Cadmium powder, 200 mesh, purity 99.99% (metals basis) (e.g. Alfa Aesar, traceable to NIST SRMs, from Thermo Fisher (Kandel) GmbH, 76870 Kandel, Germany, Order No. 11353)

- Multi-element standard (MES), 10 mg/l, matrix per volume: 5% HNO_3 per 125 ml (e.g. from PerkinElmer LAS, 63110 Rodgau, Germany, Order No. N9301720)

- Multi-element quality control standard (QC33), 100 mg/l for 33 elements (e.g. ARISTAR for ICP, traceable to NIST SRMs, including certificate of analysis, from VWR International GmbH, 64295 Darmstadt, Germany, Order No. 84791.180)

- Argon 5.0 (purity ≥ 99.999%)

- Helium 6.0 (purity 99.9999%)

2.3 Solutions

The following solutions were prepared using the chemicals listed in Section 2.2:

Acid digestion mixture: solution made of 65% nitric acid and 25% hydrochloric acid 2 : 1 (v/v) (Pitzke et al. 2018 c, 2020) 1400 ml of 65% nitric acid are placed into a 2.5-litre quartz bottle and mixed with a solution of 130 ml ultrapure water and 570 ml 30% hydrochloric acid.

Acid mixture for the preparation of the calibration and quality control samples: solution of 22% nitric acid and 4.2% hydrochloric acid
To prepare 50 ml of the mixture, 25 ml of ultrapure water are measured out, 25 ml of the above-described acid digestion mixture are added and the vessel is briefly shaken.

Dilution solution for the dilution and stabilisation of samples and standards: solution of 0.67–0.70% nitric acid 1.5 litres of ultrapure water are placed into a 2-litre PFA vessel. 20 ml of 67–70% nitric acid are added, the vessel is filled to 2 litres with ultrapure water and shaken.

Spiking solutions for precision assessment:
The spiking solutions are prepared with the single-element standards listed in Section 2.2 (see Table 1). The preparation of the spiking solutions is described in detail in Section 6.1.

Tab. 1   Element concentrations of the prepared spiking solutions

Spiking solution	Concentration				
	[mg As/l]	[µg Be/l]	[mg Cd/l]	[mg Co/l]	[mg Ni/l]
1	20		4.0	12	
2	398		48	240	
3		144			14.4

Tab. 1 *(continued)*

Spiking solution	Concentration				
	[mg As/l]	[µg Be/l]	[mg Cd/l]	[mg Co/l]	[mg Ni/l]
4		720			72
5		2880			288

Acid-stabilised solutions containing metals in concentrations above 1 mg/l are stable for a storage period of at least four weeks. Acid-stabilised solutions containing metals in concentrations between 0.1 and 1 mg/l are stable for a storage period of at least two weeks. Acid-stabilised solutions containing metals in concentrations below 0.1 mg/l should not be used for more than two days. These are the recommended shelf-lives.

Calibration and control samples must be freshly prepared every working day.

3   Sampling

Before samples are taken, the filter batch must be checked for metals to determine whether the filters fulfil the minimum requirements to ensure the effectiveness of the measurement procedures.

The membrane filter (Ø 37 mm) and the supporting sieve are placed into the filter capsule and the capsule is then inserted into the sampling head for sampling the inhalable particle fraction (GSP10) or the respirable particle fraction (FSP10). The sampling head is connected to the pump. The volumetric flow rate is set to 10 l/min. The definition of the inhalable or respirable dust is fulfilled at this volumetric flow rate (DIN 1993). At a sampling period of two hours, this corresponds to an air sample volume of 1.2 m³.

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.

The flow rate must be checked for constancy after sampling. If the deviation from the adjusted flow rate is larger than ± 5%, further samples should be taken (see DGUV Information 213-500 "General Part", Section 3 (DGUV 2015)).

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

4   Analytical determination

4.1   Sample preparation

Ceramic tweezers are used to carefully fold the loaded membrane filter and transfer it to a 25-ml digestion vessel. The filter is pressed down to the bottom of the vessel with a glass rod. 10 ml of the standard acid digestion mixture are added to the filter. An air cooler is attached to the vessel, which is then placed in a heating block thermostat and heated for two hours to boiling (block temperature: approx. 135 °C). After cooling to a temperature of approx. 50 °C, 10 ml of ultrapure water are carefully added through the air cooler to simultaneously rinse the cooler and dilute the solution, which will be slightly viscous in some cases. The solution is again heated to boiling. After cooling, the air cooler and the glass rod are removed, the digestion vessel is sealed with a polyethylene stopper and the volume of the sample solution is read off. The 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 polypropylene vessels. A dispenser system is used to add the internal standard and to fill the vessels to 10 ml with dilution solution (see Section 2.3), (measurement solution) (Pitzke et al. 2018 c, 2020).

A blank value is determined for each series of samples. For this purpose, all sample preparation and analysis steps are carried out with at least two empty filters from the same batch. The blank value that is obtained must lie within three standard deviations of the mean blank value determined during the development of the method. If this is not the case, a new mean blank value must be determined as described in Section 6.3.

4.2 Operating conditions

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

Apparatus:	Quadrupole ICP mass spectrometer, Agilent 7900 with SPS4 autosampler, Agilent Technologies Deutschland GmbH, Waldbronn, Germany
Plasma parameters:	Optimised for robust plasma conditions and samples/matrices of largely unknown composition (CeO/Ce ≤ 1.5%; Ce^{++}/Ce ≤ 1.5%)
RF power:	1550 W
Nebuliser:	MicroMist, concentric, quartz
Nebuliser chamber:	Nebuliser with Scott double-pass spray chamber, cooled
Injector:	Quartz, inner diameter 1.5 mm
Flow rate:	Sample solution: 0.4 ml/min
Carrier gas:	1.02 l/min
Detector:	Secondary electron multiplier (SEM)
Interference minimisation:	Optimisation of existing cell modes (see Table 2) with respect to potential molecular interference
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 solutions (see Sections 5.1, 5.2 and 5.3).

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.

All solutions must be freshly prepared every working day, particularly the calibration solutions and the quality control samples (see Sections 5.2 and 5.3). The spectrometric modes and possible sources of interference are given in Table 2.

Tab. 2 Spectrometric modes

Element	Mode	Isotope	Main source of interference
Arsenic	He collision mode	^{75}As	e.g. ^{40}Ar^{35}Cl, ^{36}Ar^{39}K
Beryllium	standard mode	^{9}Be	–
Cadmium	He collision mode	^{111}Cd	e.g. ^{95}Mo^{16}O$^+$, ^{39}K$_2$^{16}O$_2$^{1}H$^+$
Cobalt	He collision mode	^{59}Co	e.g. ^{43}Ca^{16}O$^+$, ^{36}Ar^{23}Na$^+$
Nickel	He collision mode	^{60}Ni	e.g. ^{44}Ca^{16}O, ^{23}Na^{37}Cl

The prepared sample solutions and filter blank solutions are analysed by ICP-MS. For this purpose, the samples and filter blank solutions are first diluted with the acid mixture described in Section 2.3 to a ratio of 1 : 10 and then mixed with internal standard. The samples are injected into the ICP-MS by autosampler and analysed under the operating conditions listed above. Each sample is analysed three times and the mean value used for the results calculation.

If metal concentrations that lie above the calibration range are detected, the sample solutions are diluted further and analysed again as described above.

The control solutions are analysed after calibration and at the end of a sequence. The results must fall within the defined limits (± 10%), otherwise the calibration must be checked and the sample solutions analysed again. This verifies the stability of the analytical devices and the accuracy of the results.

5 Evaluation

5.1 Internal standards (ISTDs)

The ISTDs must not contain any constituent elements of the samples. The ISTDs listed here were used to determine the characteristics of the method. Other internal standards may be used.

ISTD stock solution: solution of 0.4 mg Sc/l, 0.4 mg Y/l, 0.75 mg Te /l and 0.1 mg Lu/l
To prepare the ISTD stock solution, the single-element standards (1000 mg/l, see Section 2.2) are pipetted into a 500-ml volumetric flask in the volumes given in Table 3. The flask is then filled to the mark with dilution solution (0.67–0.70% nitric acid, see Section 2.3) and shaken.

Tab. 3 Preparation of the ISTD solution

Element in the standard solution	Volume of the single-element standard solution [ml]	Concentration of the ISTD solution [mg/l]
Sc	0.2	0.4
Y	0.2	0.4
Te	0.75	1.5
Lu	0.1	0.2

0.1 ml of the ISTD stock solution is added to all solutions, including the calibration, quality control and sample solutions (total volume: 10 ml). All measurement solutions thus contain scandium and yttrium in concentrations of 4 µg/l, tellurium in a concentration of 15 µg/l and lutetium in a concentration of 2 µg/l.

5.2 Calibration

The calibration must be performed every working day. To derive the calibration functions, two intermediate dilutions are prepared from the multi-element standard (MES, 10 mg/l) (see Section 2.2). In the following, these are referred to as multi-element stock solution 1 (100 µg/l) and multi-element stock solution 2 (1 µg/l).

Multi-element stock solution 1: solution of 100 µg element/l in 0.67–0.70% nitric acid
To prepare stock solution 1, 100 µl of the MES are pipetted into a 15-ml polypropylene vessel. The vessel is filled to 10 ml with dilution solution (0.67–0.70% nitric acid) using a dispenser system and then shaken.

Multi-element stock solution 2: solution of 1 µg element/l in 0.67–0.70% nitric acid
To prepare stock solution 2, 100 µl of stock solution 1 are added by pipette into a 15-ml-polyproplyene vessel. The vessel is filled to 10 ml with dilution solution (0.67–0.70% nitric acid) using a dispenser system and then shaken.

Calibration solutions:

To prevent non-spectral interference, the calibration is performed after correcting for matrix effects, i.e. the acid concentration in the calibration standards is equivalent to a 1 : 10 dilution of the digestion solutions.

For the calibration solutions, 1 ml of the acid mixture for the preparation of the calibration and quality control samples from Section 2.3 and 100 µl of the internal standard solution are thus added to ten 10-ml volumetric flasks each.

A pipette is used to measure out the MES as well as the multi-element stock solutions 1 and 2 in the volumes listed in Table 4. The flasks are then filled with dilution solution for the dilution and stabilisation of samples and standards (0.67–0.70% nitric acid) to a total volume of 10 ml and shaken.

Tab. 4   Dilutions used to derive the calibration functions (total volume: 10 ml)

Calibration solution	Volume multi-element standard [µl]	Volume multi-element stock solution 1 [µl]	Volume multi-element stock solution 2 [µl]	Concentration [µg/l]
0	–	–	–	0
1	–	–	100	0.01
2	–	–	500	0.05
3	–	10	–	0.1
4	–	50	–	0.5
5	–	100	–	1.0
6	–	500	–	5.0
7	–	1000	–	10
8	50	–	–	50
9	100	–	–	100

The standards are analysed by ICP-MS under the operating conditions described in Section 4.2

The analytes are identified based on their mass-to-charge ratio and are plotted against the analyte concentrations. The calibration functions are linear under the given conditions.

Higher metal concentrations in the sample solution can be determined by carrying out suitable dilution steps. Due to potential spectral interference, signals must always be assessed carefully. If necessary, interferences must be minimised through the application and optimisation of collision cell parameters.

5.3   Quality control

Quality control procedures are performed during an analytical run using commercially available solutions (multi-element quality control standard, see Section 2.2). The aim is to verify the accuracy of the calibration and the stability over time every working day and over the entire measurement period.

Quality control stock solution: solution of 100 µg element/l in 0.67–0.70% nitric acid
Quality control samples are obtained by preparing a 100 µg/l quality control stock solution. For this purpose, 10 µl of the multi-element quality control standard (QC33) are pipetted into a 10-ml volumetric flask. The flask is filled to the mark with the dilution solution (0.67–70% nitric acid) described in Section 2.3.

Quality control solutions:

Like the calibration solutions, the quality control samples are corrected for matrix effects, i.e. the acid concentration is equivalent to a 1:10 dilution of the digestion solutions.

For quality control solutions 1 to 3, 1 ml of the acid mixture for the preparation of the calibration and quality control samples from Section 2.3 and 100 µl of the internal standard solution are thus added to three 10-ml volumetric flasks each. A pipette is used to measure out the quality control stock solution in the volumes listed in Table 5. The flasks are then filled with ultrapure water to a total volume of 10 ml and shaken.

To prepare quality control solution 4, 10 µl of QC33, 1 ml of the acid mixture for the preparation of the calibration and quality control samples from Section 2.3 and 100 µl of the internal standard solution are pipetted into a 10-ml volumetric flask, which is then filled with ultrapure water to a total volume of 10 ml and shaken.

Table 5 shows which quality control solutions are used as benchmarks for the elements in this method.

Tab. 5 Dilutions for the preparation of the quality control (QC) samples

QC solution	Volume QC stock solution [μl]	Volume QC33 [μl]	Concentration [μg element/l]	Used as benchmark for				
				As	Be	Cd	Co	Ni
1	10	–	0.1		X	X	X	X
2	100	–	1	X	X	X	X	X
3	1000	–	10	X		X	X	X
4	–	10	100	X				

5.4   Calculation of the analytical result

The analyte concentration in the workplace air is calculated based on the analyte concentration in the measurement solution that was determined by a software programme. The data analysis programme uses the calculated calibration function for this purpose. The analyte concentration in the workplace air is calculated from the analyte concentrations taking the corresponding dilutions and the air sample volume into account.

The mass concentrations of analyte in the air sample are calculated in μg/m^3 using Equation 1.

$$\rho = \frac{(c \times fv_c - c_{blank} \times fv_{cblank}) \times V_{sol}}{\eta \times V_{air}} \tag{1}$$

Where:

ρ is the mass concentration of the analyte in the air sample in μg/m^3

c is the concentration of analyte in the measurement solution in μg/l

fv_c is the dilution factor of the sample (generally a dilution of 1 : 10)

c_{blank} is the concentration of the blank value (mean value) of the analyte in the measurement solution in μg/l

fv_{cblank} is the dilution factor of the blank value (generally a dilution of 1 : 10)

V_{sol} is the volume of the prepared sample solution in l

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

η is the recovery (= 1.0)

6   Reliability of the method

The characteristics of the method were calculated according to DIN EN 482 (DIN 2021), DIN EN ISO 21832 (DIN 2020), ISO 20581 (DIN 2016), DIN 32645 (DIN 2008) and TRGS 402 (AGS 2023 b).

6.1   Precision

The precision of the method was determined by spiking twelve membrane filters each with three different masses of the metals being evaluated using the spiking solutions mentioned in Section 2.3.

Spiking solution 1: solution of 20 mg As/l, 12 mg Co/l and 4 mg Cd/l
1 ml of the arsenic standard solution, 0.6 ml of the cobalt standard solution and 0.2 ml of the cadmium standard solution listed in Section 2.2 are pipetted into a 50-ml volumetric flask. The solution is brought to volume by adding the

dilution solution (0.67–0.70% nitric acid) to the flask, which was then shaken. Spiking solution 1 was used for spike tests at 0.2 and 0.5 times the AC.

Spiking solution 2: solution of 398 mg As/l, 240 mg Co/l and 48 mg Cd/l
4 ml of the arsenic standard solution, 2.4 ml of the cobalt standard solution and 0.48 ml of the cadmium standard solution listed in Section 2.2 are pipetted into a 10-ml volumetric flask, brought to volume with the dilution solution (0.67–0.70% nitric acid) and then shaken. Spiking solution 2 was used for the spike tests at two times the TC of these elements.

Spiking solution 3: solution of 144 µg Be/l and 14.4 mg Ni/l
0.72 ml of the beryllium standard solution and 0.72 ml of the nickel standard solution listed in Section 2.2 are pipetted into a 50-ml volumetric flask, brought to volume with dilution solution (0.67–0.70% nitric acid) and shaken. This spiking solution was used for the tests at 0.1 times the OELV.

Spiking solution 4: solution of 720 µg Be/l and 72 mg Ni/l
0.72 ml of the beryllium standard solution and 0.72 ml of the nickel standard solution listed in Section 2 were pipetted into a 10-ml volumetric flask, brought to volume with dilution solution (0.67–0.70% nitric acid) and shaken. Spiking solution 4 was prepared for the spike tests at 0.5 times the respective OELV.

Spiking solution 5: solution of 2.88 mg Be/l and 288 mg Ni/l
2.88 ml of the beryllium and nickel standard solutions listed in Section 2.2 are pipetted each into a 10-ml volumetric flask, brought to volume with dilution solution (0.67–0.70% nitric acid) and shaken. Spiking solution 5 was prepared for the spike test at 2 times the respective OELV.

The filters were spiked with defined volumes of the spiking solutions described above and then dried at room temperature for 24 hours. After spiking, the filters underwent the same digestion, preparation and analysis steps as described in Sections 4.1, 4.2 and 5 for the sample solutions.

At an air sample volume of 1200 l, the spiked amounts of each element are equivalent to the air concentrations listed in Table 6.

Prior to analysis by ICP-MS, the digestion solutions were diluted by a factor of 10 with the dilution solution described in Section 2.3. In addition, a complete analytical run was carried out with two empty filters.

The data for precision given in Table 6 are based on these results.

Tab. 6   Precision data

Element	Spiking solution	Spiking volume [µl]	Spiked mass [µg]	Concentration[a] [µg/m³]	Relative standard deviation [%]
Arsenic	1	10	0.20	0.17	4.2
	1	25	0.50	0.42	2.2
	2	50	20	17	1.3
Beryllium	3	50	0.0070	0.0060	2.7
	4	50	0.035	0.030	2.3
	5	50	0.15	0.12	4.4
Cadmium	1	10	0.040	0.033	2.1
	1	12	0.10	0.080	2.7
	2	50	2.5	2.0	1.8
Cobalt	1	10	0.12	0.10	2.0
	1	25	0.30	0.25	2.2
	2	50	12	10	1.0

Tab. 6   *(continued)*

Element	Spiking solution	Spiking volume [µl]	Spiked mass [µg]	Concentration[a] [µg/m³]	Relative standard deviation [%]
Nickel	3	50	0.70	0.60	2.3
	4	50	3.5	3.0	3.0
	5	50	15	12	1.7

[a] The concentration is calculated on the basis of a 2-hour sampling period at a volumetric flow rate of 10 l/min.

A mean recovery of 97% was determined for arsenic, 111% for beryllium, 101% for cadmium, 98% for cobalt and 101% for nickel.

6.2   Recovery

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

Certified metals and metal compounds (see Section 2.2) were used to evaluate the described sample preparation method with regard to the analytical recovery and the reproducibility of the method. Recovery experiments were performed with arsenic trioxide, beryllium oxide, cadmium powder, cobalt powder and nickel powder.

As the carcinogenic metals intended for analysis are usually collected in the ultratrace range and therefore reliable weighing of reference materials is difficult, the following procedure was chosen:

Referring to the general threshold limit value for dust of 10 mg/m³ (inhalable fraction) and based on an air sample volume of 1.2 m³, six samples were prepared by mixing approx. 12 mg of the compounds described in Table 6 in powder form with 10 ml of acid digestion mixture. The samples were subjected to the complete digestion process and then diluted to the range of the analytical procedure as specified in Table 7. Correction by the recovery is not required for the analytes described here.

The recoveries for all reference materials mentioned above are given as mean values in Table 7.

Tab. 7   Mean recovery for carcinogenic metals with n = 6 determinations

Element	Tested compound	Mean recovery [%]	Mean relative standard deviation [%]	Dilution factor
Arsenic	Arsenic trioxide	102	2.7	10 000
Beryllium	Beryllium oxide	101	6.3	1 000 000
Cadmium	Cadmium	92.3	3.1	100 000
Cobalt	Cobalt	88.8	2.6	100 000
Nickel	Nickel	94.8	1.7	100 000

6.3   Limit of quantification

During method development, the limit of quantification was calculated based on the blank value method described in DIN 32645 (DIN 2008). For this purpose, ten unused membrane filters were processed through all preparation and analysis steps of the method and the results were used to determine the limit of quantification (see Table 8). The mean value, the analyte blank values obtained from the filters, reagents and vessels used in the experiments and the corresponding standard deviation were calculated. The relative limit of quantification is calculated using ten times

the standard deviation of the blank values in the measurement solution, the digestion volume of 20 ml, the dilution factor of 10 and an air sample volume of 1.2 m^3.

Tab. 8   Absolute and relative limits of quantification (LOQ)

Element	Absolute LOQ [µg]	Relative LOQ[a] [µg/m^3]
Arsenic	0.0017	0.0014
Beryllium	0.00035	0.00029
Cadmium	0.013	0.011
Cobalt	0.035	0.029
Nickel	0.13	0.11

[a] The LOQ is calculated on the basis of a 2-hour sampling period at a volumetric flow rate of 10 l/min, 20 ml sample solution and a dilution factor of 10.

6.4   Storage stability

The storage stability of the loaded membrane filters was analysed by spiking the filters with the spiking solutions described in Section 2.3.

The filters were spiked with the metals being analysed by applying the corresponding spiking solution. The spiking solution used in each case is listed in Table 9 together with the corresponding spiking volumes.

Tab. 9   Spiking scheme used for the evaluation of storage stability

Element	Spiking solution	Spiking volume [µl]	Spiked mass [µg]	Concentration[a] [µg/m^3]
Arsenic	1	10	0.20	0.17
	2	50	20	17
Beryllium	3	50	0.0070	0.0060
	5	50	0.15	0.12
Cadmium	1	10	0.04	0.033
	2	50	2.5	2.0
Cobalt	1	10	0.12	0.10
	2	50	12	10
Nickel	3	50	0.70	0.60
	5	50	15	12

[a] The concentration is calculated on the basis of a 2-hour sampling period at a volumetric flow rate of 10 l/min.

Over a period of four weeks, three filters each were subjected to the entire preparation and analysis procedure on two measurement days. The recoveries for both metal concentrations were stable over the investigated time period.

6.5   Selectivity

The selectivity of the method depends above all on the choice of isotope, on the absence of spectral interference and on the minimisation of non-spectral interference.

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 ≤ 2%) as well as by applying the described collision cell technology followed by kinetic energy discrimination.

In samples of largely 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 in order to achieve valid results.

A small number of dusts at the workplace (e.g. from electronic waste) are known to cause interference with arsenic due to high concentrations of doubly-charged $^{150}Nd^{2+}$ and $^{150}Sm^{2+}$ ions in the plasma. Therefore, isotopes of these metals should be included in the analysis at least as monitor ions.

6.6   Uncertainty

The expanded uncertainty was determined by estimating all relevant influencing parameters. The two main sources of uncertainty in the measurement results are uncertainties in the sampling procedure and 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 respirable dusts according to Appendix C of DIN EN ISO 21832 and ISO 20581 (DIN 2016, 2020). An uncertainty of 9.3% was calculated for the inhalable particle fraction by combining random and non-random uncertainties after sampling for two hours at a volumetric flow rate of 10 l/min. The uncertainty arising from sampling was determined to be 11.7% for the respirable particle fraction.

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 (Qualisyst n.d.) was used to determine the concentration-dependent analytical uncertainties for this method.

The combined uncertainties for the entire method were calculated by combining the contributions from all sources of uncertainty. The percentages listed in Table 10 for the expanded uncertainties (U) for the entire method at a volumetric flow rate of 10 l/min and sampling period of 2 hours were obtained by multiplying these values with the expansion factor k = 2. The expanded uncertainties reflect the worst case, i.e. the concentrations in the respective work area that lead to the highest uncertainty values (in each case, the lowest analysed concentration for the respirable particle fraction). For higher concentrations within the given measurement range, the expanded uncertainties are even lower than the values listed in Table 10.

Tab. 10   Expanded uncertainty (U) with n = 6 determinations

Element	Expanded uncertainty (U) [%]
Arsenic	28
Beryllium	25
Cadmium	23
Cobalt	21
Nickel	24

6.7   Comparison of open hot-block digestion with microwave-assisted pressure digestion

Experiments were carried out to compare the open hot-block digestion described here with the microwave-assisted pressure digestion that was included as an alternative digestion method given in Pitzke et al. (2018 c, 2020).

For this purpose, dusts with different matrices and compositions that were deposited at actual workplaces were collected and processed to obtain particle sizes ≤ 100 µm. By convention, this is considered equivalent to the inhalable particle fraction (DIN 1993). Solutions were prepared with the processed dusts using either the open hot-block digestion

or microwave-assisted pressure digestion described in the reference works. The concentrations of metals in the solutions were quantitatively analysed by ICP-MS after being diluted by an appropriate factor.

The results of the quantitative analysis showed that the concentrations of metals obtained using the two different digestion methods were very similar. The results have been published in various publications (Pitzke et al. 2018 a, b; Schwank et al. 2019 a, b).

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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