The MAK-Collection for Occupational Health and Safety

GMS PUBLISSO ZB MED-Publikationsportal Lebenswissenschaften

Platinum – Determination of platinum in workplace air using atomic absorption spectrometry (AAS)

Air analysis method – Translation of the German version from 2022

A. Woznica[1]
R. Hebisch[2,*]
P. Möller[3]
K. Pitzke[3]
A. Hartwig[4,*]
MAK Commission[5,*]

1 *Method development, Federal Institute for Occupational Safety and Health (BAuA), Friedrich-Henkel-Weg 1–25, 44149 Dortmund, Germany*

2 *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*

3 *External verification, Institute for Occupational Safety and Health (IFA) of the German Social Accident Insurance (DGUV), Alte Heerstraße 111, 53757 Sankt Augustin, 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: R. Hebisch (luftanalysen-dfg@baua.bund.de), A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)*

Keywords

platinum; air analyses; analytical method; workplace measurement; hazardous substance; atomic absorption spectrometry; GF-AAS; high-pressure microwave digestion system; quartz fibre filter

Abstract

The analytical method described here permits the determination of platinum in the inhalable particle fraction in workplace air in a concentration range of one tenth up to twice the currently valid Occupational Exposure Limit Value (OELV) in Germany of 1 mg/m^3 in the inhalable particle fraction.

Sampling is performed by drawing a defined volume of air through a quartz fibre filter using a suitable pump and sampling head. The flow rate is set to 10 l/min at a sampling period of 2 h. The platinum particles deposited on the filter are determined by a graphite furnace atomic absorption spectrometer (GF-AAS) after acid digestion using a high-pressure microwave digestion system. Quantitative evaluation is based on an external multiple-point calibration. The limit of quantification is 15 µg/l and 30 µg/m^3 for a sampling volume of 1200 l and a sampling period of 2 h. The mean recovery is 95% and the expanded uncertainty for the validation range of 0.1 to 2 mg/m^3 is 25–29% for the inhalable particle fraction.

Citation Note:
Woznica A, Hebisch R, Möller P, Pitzke K, Hartwig A, MAK Commission. Platinum – Determination of platinum in workplace air using atomic absorption spectrometry (AAS). Air analysis method – Translation of the German version from 2022. MAK Collect Occup Health Saf. 2022 Sep;7(3):Doc065. https://doi.org/10.34865/am744006e7_3or

Manuscript completed:
12 Oct 2021

Publication date:
30 Sep 2022

Method number	1
Application	Air analysis
Analytical Principle	Atomic absorption spectrometry (AAS)

1 Characteristics of the method

Repeatability for control solutions:	Standard deviation (rel.): s = 1.9–3.2% at concentrations of 2.4 mg/l, 24 mg/l and 48 mg/l
Repeatability for sample solutions:	Standard deviation (rel.): s = 2.0–5.6% at concentrations of 2.4 mg/l, 24 mg/l and 48 mg/l
Reproducibility:	Standard deviation (rel.): s = 0.9–4.3% at spiked concentrations of 0.12 mg Pt/filter, 1.2 mg Pt/filter and 2.4 mg Pt/filter
Expanded uncertainty:	25–29% for the inhalable particle fraction in the concentration range of 0.1 to 2 mg/m^3
Limit of quantification:	15 µg/l 30 µg/m^3 for an air sample volume of 1200 l, a sample volume of 50 ml and a sampling period of 2 h
Recovery:	η = 0.99 (for 0.12 mg Pt/filter); η = 0.95 (for 1.2 mg Pt/filter) and η = 0.91 (for 2.4 mg Pt/filter)
Sampling recommendations:	Sampling period: 2 h Air sample volume: 1200 l

2 Description of the substances

Platinum [7440-06-4]

Platinum is a chemical element with the chemical symbol Pt, the atomic number 78 and a relative atomic mass of 195.09 u. It has a high density (21.45 g/cm^3) and is a valuable, malleable, ductile, grey-white transition metal with a melting point of 1772 °C and a boiling point of 4350 °C.

Platinum is a precious metal with a high resistance to corrosion, limited reactivity and often occurs in its metallic form. Due to its rarity (classified as 76th in the list of the most common elements) only small amounts are extracted annually (Statista Research Department 2022). It is used in the manufacture of jewellery, catalytic converters for vehicles, laboratory devices, tooth implants and contact materials.

For activities involving platinum as a metal in inhalable particulate form the OELV is 1 mg/m^3 (inhalable particle fraction). No short-term exposure limit has been assigned. Therefore, excursion by a factor of eight for 15 minutes, i.e. 8 mg/m^3, is permissible (AGS 2016). Currently no limit values or evaluation criteria exist for activities involving exposure to platinum compounds with sensitising potential (halogenated platinum compounds).

3 General principles

This analytical method permits the determination of platinum dusts in the workplace air in a concentration range of one tenth up to twice the currently valid OELV of 1 mg/m^3 (inhalable particle fraction) (AGS 2021).

A flow-regulated pump draws a defined volume of air at 10 l/min through a quartz fibre filter for the sampling procedure. The platinum is deposited in the form of the inhalable particle fraction on the filter in the GSP sampling head and it is determined using a graphite furnace atomic absorption spectrometer (GF-AAS) after acid digestion with a high-pressure microwave digestion system. The quantitative evaluation is based on an external multiple-point calibration, whereby the concentrations of platinum in the reference standards are plotted versus the peak areas obtained by means of an integration program.

4 Equipment, chemicals and solutions

All glassware must be pre-rinsed with dilute nitric acid (approx. 3%) and ultrapure water before use in order to ensure that all vessels are free of any trace of metals.

4.1 Equipment

For sampling:

- Pump for personal air sampling, flow rate of 10.0 l/min (e. g. SG10-2, from GSA Gesellschaft für Schadstoffanalytik mbH, 40880 Ratingen, Germany)
- Sampling head for personal sampling for the inhalable particle fraction (GSP) with an intake cone for 10 l/min (e. g. from DEHA Haan & Wittmer, 71296 Heimsheim, Germany)
- Filter cassettes with metal supporting sieve and cap with a diameter of 37 mm for the GSP sampling head (e. g. from DEHA Haan & Wittmer, 71296 Heimsheim, Germany)
- Quartz fibre filter, 37 mm diameter (e. g. MN QF-10, from Macherey-Nagel GmbH and Co. KG, 52355 Düren, Germany)
- Flow meter (e. g. TSI Flowmeter 4146, from TSI Incorporated, 52068 Aachen, Germany)
- Vacuum desiccator made of borosilicate glass for storage

For sample preparation and analysis:

- High-pressure microwave digestion system with digestion vessels and seals made of PTFE (e. g. MarsXpress, from CEM, 47475 Kamp-Lintford, Germany)
- Heating block made of graphite with control unit with 48 positions for 50 ml tubes (e. g. DigiPREP MS, from S-prep GmbH, 88662 Überlingen, Germany)
- Atomic absorption spectrometer with graphite furnace and autosampler (e. g. ZEEnit 700P from Analytik Jena GmbH, 07745 Jena, Germany)
- Transversely heated graphite furnace with platform (e. g. from Analytik Jena GmbH, 07745 Jena, Germany)
- Platinum hollow cathode lamp (e. g. from Analytik Jena GmbH, 07745 Jena, Germany)
- Ultrapure water unit (e. g. Millipore-Q-Gradient® with Elix® 3UV, from Merck, 64293 Darmstadt, Germany)
- Variable piston pipettes, 10 to 100 µl, 100 to 1000 µl and 250 to 2500 µl (e. g. Reference 2®, from Eppendorf AG, 22366 Hamburg, Germany)

- Bottle dispenser attachment, 1 to 10 ml (e. g. Dispensette S® analog, from BRAND GmbH & Co. KG, 97877 Wertheim, Germany)
- Analytical balance (e. g. XPE-20S Delta Range® from Mettler-Toledo GmbH, 35396 Gießen, Germany)
- Chromafil® syringe filter, pore width 0.45 µm, diameter 25 mm (e. g. from Carl Roth GmbH & Co. KG, 76185 Karlsruhe, Germany)
- Disposable syringes, 5 ml, made of polyethylene with Luer lock connection
- Disposable digestion vessels, 50 ml, and accessories made of polyethylene (e. g. DigiTube® from S-prep GmbH, 88662 Überlingen, Germany)
- Volumetric flasks, 1000 ml (e. g. from BRAND GmbH & Co. KG, 97877 Wertheim, Germany)
- Ceramic tweezers
- Autosampler vials and Pasteur pipettes, 7 ml, graduated, made of polyethylene

4.2 Chemicals

- Platinum powder, purity 99.999%, 1 g (e. g. from Acros Organics; 2440 Geel, Belgium, Order No. 193710010)
- Platinum standard solution, 100 ml, 1000 mg Pt/l in 2 M hydrochloric acid (H_2PtCl_6) (e. g. Certipur® standard for the AAS, Supelco®, from Merck KGaA, 64293 Darmstadt, Germany, Order No. 1.70219.0100)
- Platinum standard solution, 50 ml, 10 000 µg Pt/ml in 20% hydrochloric acid (e. g. Specpure® standard for the ICP, from Thermo Fisher (Kandel) GmbH, 76185 Karlsruhe, Germany, Order No. 14397)
- Nitric acid (65%), 1 l, Suprapur® (e. g. from Merck KGaA, Darmstadt, Germany, Order No. 1.00441)
- Hydrochloric acid (30%), 1 l, Suprapur® (e. g. from Merck KGaA, Darmstadt, Germany, Order No. 1.00318)
- Ultrapure water, p ≥ 18 MΩ · cm at 25 °C
- Argon 5.0 (purity at least 99.999%)

4.3 Spiking solutions for the validation

Platinum Spiking Solution 1: (10 000 µg/ml):
The platinum standard solution of 10 000 µg/ml is used undiluted as Spiking Solution 1.

Platinum Spiking Solution 2: (20 000 µg/ml):
1000 ± 15 mg of the platinum powder (99.999%) are weighed into a 50 ml disposable digestion vessel and are digested with 6 ml of nitric acid (65%) and 18 ml of hydrochloric acid (30%) in the DigiPREP MS graphite heating block until no residue remains. The temperature program used for this purpose is shown in Table 1. After cooling the digestion solution, the digestion vessel is filled to the mark with ultrapure water, sealed and shaken.

Tab. 1 Temperature program of the DigiPREP MS graphite heating block

Temperature program	Level 1	Level 2
Heating rate	15 min	15 min
Dwell time	5 min	20 min
Target temperature:	50 °C	100 °C

4.4 Calibration standards

Blank Value Solution 1 (nitric acid solution 0.5%): used for dilution of the sample and control solutions as well as a rinsing solution for the autosampler.
Approx. 7.5 ml of nitric acid (65%) are pipetted into a 1000-ml volumetric flask, into which approx. 500 ml of ultrapure water have been previously placed. The volumetric flask is then filled to the mark with ultrapure water, sealed and shaken.

Blank Value Solution 2 (nitric acid solution 1%): for stabilisation of the calibration and control solutions
Approx. 15 ml of nitric acid (65%) are pipetted into a 1000-ml volumetric flask, into which approx. 500 ml of ultrapure water have been previously placed. The volumetric flask is then filled to the mark with ultrapure water, sealed and shaken.

Platinum Working Solution 1: 1000 µg/l
0.05 ml of the platinum standard solution (1000 mg/l) are pipetted into a 50-ml disposable digestion vessel, into which approx. 30 ml of Blank Value Solution 2 have been previously placed. The digestion vessel is then filled to the mark with Blank Value Solution 2, sealed and shaken.

Platinum Working Solution 2: 100 µg/l
5.0 ml of Platinum Working Solution 1 are pipetted into a 50-ml disposable digestion vessel, into which approx. 30 ml of blank value solution 2 have been previously placed. The digestion vessel is then filled to the mark with Blank Value Solution 2, sealed and shaken.

Calibration standards

Eight calibration standards are prepared using the autosampler from both of the platinum working solutions and Blank Value Solution 1 according to the specifications in Table 2.

Tab. 2 Autosampler pipetting scheme for preparation of the eight calibration standards

Calibration standards	Working Solution	Concentration [µg platinum/l]	Volume of Blank Value Solution 1 [µl]	Volume of platinum calibration solution [µl]
Pt Blank Value		0	20	0
Pt Standard 1	2	30	14	6
Pt Standard 2	2	40	12	8
Pt Standard 3	2	60	8	12
Pt Standard 4	2	100	0	20
Pt Standard 5	1	300	14	6
Pt Standard 6	1	500	10	10
Pt Standard 7	1	750	5	15
Pt Standard 8	1	1000	0	20

4.5 Control solutions (QC standards)

The control solutions are prepared by dilution of Platinum Spiking Solution 1 (10 000 µg/ml) as follows:

Platinum Control Solution 1 (2.4 mg/l):
12 µl of Platinum Spiking Solution 1 (10 000 µg/ml) are pipetted into a 50-ml disposable digestion vessel, into which approx. 30 ml of Blank Value Solution 2 have been previously placed. The digestion vessel is then filled to the mark with Blank Value Solution 2, sealed and shaken.

Platinum Control Solution 2 (24 mg/l):
120 µl of Platinum Spiking Solution 1 (10 000 µg/ml) are pipetted into a 50 ml disposable digestion vessel, into which approx. 30 ml of Blank Value Solution 2 have been previously placed. The digestion vessel is then filled to the mark with Blank Value Solution 2, sealed and shaken.

Platinum Control Solution 3 (48 mg/l):
240 µl of Platinum Spiking Solution 1 (10 000 µg/ml) are pipetted into a 50 ml disposable digestion vessel, into which approx. 30 ml of Blank Value Solution 2 have been previously placed. The digestion vessel is then filled to the mark with Blank Value Solution 2, sealed and shaken.

5 Sampling and sample preparation

5.1 Sampling

Sampling can be carried out as stationary or personal sampling. The caps of the filter cassette are removed and a quartz fibre filter (Ø = 37 mm) with a supporting sieve is placed into the GSP sampling system intake cone for 10 l/min. A flow rate of 10 l/min is then set. This is equivalent to an air sample volume of 1200 l for a sampling period of 2 hours.

After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, the sample must be discarded and the measurement repeated as stipulated in DIN EN ISO 13137 (DIN 2014). The filter cassette with the loaded filter is sealed with the caps designated for this purpose and transported to the laboratory for analysis. The air samples can be stored at room temperature in the desiccator made of borosilicate glass until analysis.

At least one blank sample (field blank) per sample series must be included. This differs from the analytical sample only in that no sample air is drawn through the filter. This blank sample is handled, stored, prepared and analysed in the same manner as the other samples.

5.2 Sample preparation

The loaded filter is carefully removed from the filter cassette using ceramic tweezers, placed into a digestion vessel made of PTFE and 3 ml of nitric acid (65%) and 9 ml of hydrochloric acid (30%) are added.

A supporting sieve is inserted into the PTFE digestion vessel and it is sealed with a cap. The field blank value is prepared in the same manner. The digestion vessels containing the samples are evenly distributed on the sample turntable of the microwave digestion device.

Digestion is carried out by increasing the microwave power to 1500 W within a period of 25 minutes and maintaining the power at this level for 15 minutes. The maximum permissible control temperature is around 210 °C. After the samples have been digested, they are left to cool in the microwave device. In this case, the quartz fibre filter is not completely digested without leaving any residue.

The digestion solution including the non-digested quartz fibre filter is carefully transferred into a 50-ml disposable digestion vessel. The vessel is then filled to the mark with ultrapure water, sealed and shaken.

The sample solution is stored at room temperature until analysis. Immediately before analysis, part of the sample solution is filtered into an autosampler vial using a syringe filter.

If the platinum concentration of the field blank value is above that of the batch blank value of the filter, then a non-loaded filter from the same laboratory batch must be checked.

The prepared samples (diluted by a factor of 50), field blank and, if applicable, a batch blank are injected by means of the autosampler and analysed.

6 AAS operating conditions

Apparatus:	Atomic absorption spectrometer ZEEnit 700P with graphite furnace and Zeeman background compensation (from Analytik Jena GmbH)
Graphite furnace:	Transversely heated graphite furnace with platform (from Analytik Jena GmbH)
Hollow cathode lamp:	Platinum
Measured wavelength:	265.9 nm
Spectral slit width:	0.2 nm
Signal evaluation mode:	Peak area
Autosampler injection volume:	20 µl
Autosampler dilution:	Factor of 50 for samples and control solutions
Rinsing / dilution solution:	Blank Value Solution 1 (nitric acid 0.5%)
Inert gas:	Argon (5.0)

The device must be switched on for at least 15 minutes to allow the lamp to warm up before measurement commences.

The temperature/time program of the graphite furnace is shown in Table 3.

Tab. 3 Temperature/time program

Program step	Furnace temperature [°C]	Ramp [°C/s]	Dwell time [s]	Rinsing gas
1 Drying	85	6	20	max
2 Drying	95	3	25	max
3 Drying	110	5	10	max
3 Pyrolysis	350	50	20	max
4 Pyrolysis	1200	300	10	max
5 Autozero	1200	0	6	stop
6 Atomisation	2200	1500	8	stop
7 Heating	2450	500	4	max

7 Analytical determination

The samples and the field blank value prepared according to Section 5.2, Blank Value Solution 2 (nitric acid 1%), the control solutions and, if necessary, a filter batch blank value are analysed by means of the AAS. For this purpose, each of the solutions is diluted in advance in the autosampler by a factor of 50 with Blank Value Solution 1 (nitric acid 0.5%) in a separate autosampler vial, then 20 µl of the diluted solution are injected into the graphite furnace and analysed under the AAS operating conditions described in Section 6. Each sample is analysed in duplicate and the resulting mean value is used for calculating the result.

The graphite furnace is heated before and after the analytical series, and a zero adjustment is performed by the software. In order to eliminate any contamination from the previous measurements, an additional purifying step by means of heating is also carried out after the calibration and the sample sequence. At the beginning and at the end of the sample sequence the control solutions are analysed as stipulated in Section 4.5 to check the calibration function. In the case of a larger series of samples it is advisable to analyse control solutions after every 15 sample measurements for quality control purposes.

8 Calibration

External calibration:

The calibration must be performed every working day. The platinum working solutions with concentrations of 100 µg/l and 1000 µg/l are prepared according to Section 4.4. The autosampler is used to dilute the working solutions with Blank Value Solution 1 (nitric acid solution 0.5%) in the concentration range of 30 to 1000 µg/l to yield the eight calibration standards as specified in Table 2. The calibration standards are analysed in duplicate in the same manner as the samples.

As shown in Figure 1, the calibration function is linear under the selected operating conditions. The degree of certainty of the calibration function must fall within defined limits ($R^2 > 0.99$), otherwise the calibration must be checked and if necessary repeated. The evaluation software installed by the manufacturer generally evaluates the calibration points and blank values to yield the concentrations of the samples directly in µg/l.

If the measurement value is above the calibration range, then an appropriately diluted aliquot must be analysed.

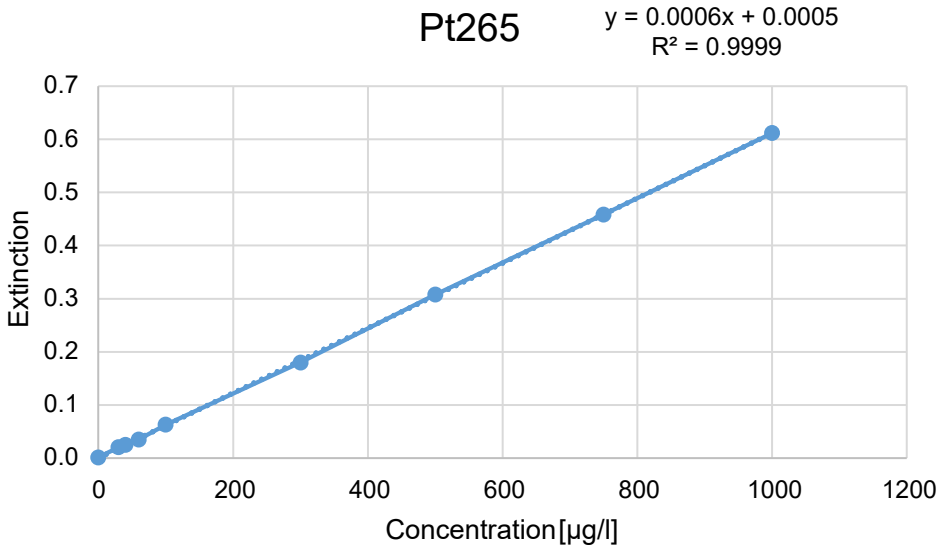

Fig. 1 Calibration function of platinum in the working range of 30 µg/l to 1000 µg/l

9 Calculation of the analytical result

The concentration of platinum in the measurement solution is calculated using the evaluation program and the linear calibration function. The concentration of platinum in the workplace air is calculated taking the corresponding dilutions, the preparation volume, the air sample volume and the recovery rate into account. The concentration of platinum in the workplace air is calculated using Equation 1 as follows:

$$\rho = \frac{((C \times f_d) - C_{blank}) \times V \times 100}{V_{Air} \times \mathrm{R} \times 1000} \quad (1)$$

where:

ρ is the mass concentration of platinum in the air sample in mg/m³
C is the concentration of platinum in the measurement solution (mean value) in µg/l
C_{blank} is the concentration of the blank value (mean value) in µg/l
f_d is the dilution factor (50 in this case)
V is the volume of the sample solution in l (0.05 in this case)
V_{air} is the air sample volume in litres
R is the recovery in %

10 Reliability of the method

The characteristics of the method were calculated as stipulated in DIN EN 482 (DIN 2021), DIN EN ISO 21832 (DIN 2020) and DIN 32645 (DIN 2008).

10.1 Repeatability

The repeatability was determined by preparing and analysing three independent control solutions according to Section 4.5 and three independent sample solutions (spiking of the filters was carried out in the same manner as shown in Table 5) with concentrations of 2.4 mg/l, 24 mg/l and 48 mg/l as stipulated in Section 5.2 on each day over a period of six days. The relative standard deviations thus determined are presented in Table 4.

Tab. 4 Determination of the repeatability

Concentration [mg/l]	Relative standard deviation of the control solution [%]	Relative standard deviation of the sample solution [%]
2.4	3.2	5.6
24	2.3	2.0
48	1.9	2.5

10.2 Recovery and reproducibility

The recovery and reproducibility were determined by spiking twelve filters with a defined volume of Platinum Spiking Solution 1 (10 000 µg/ml) or 2 (20 000 µg/ml) from Section 4.3 according to Table 5 at three predefined concentrations each, followed by storage at room temperature for 24 hours. In each case six of these filters in a series were prepared without sampling according to Section 5.2 for determination of the conversion rate. Laboratory air was drawn through the other six filters over a time period of 2 hours at a flow rate of 10 l/min. These were then also prepared (see Section 5.2) and analysed.

Tab. 5 Sample composition for the determination of the conversion rate (without sampling) and the recovery (with sampling)

Spiked platinum per filter	Platinum concentration in the air	Number	Spiking Solution 1 (10 000 µg/ml)]	Spiking Solution 2 (20 000 µg/ml)]
[mg]	[mg/m³]		[µl]	[µl]
0.12	0.1	6	12	–
1.20	1	6	–	60
2.40	2	6	–	120

As prescribed in Table 6, quality control samples (QC samples) were prepared by pipetting volumes of Platinum Spiking Solution 1 or 2 into six 50 ml disposable digestion vessels, into which approx. 30 ml of Blank Value Solution 2 have been previously placed. The digestion vessels were filled to the mark with Blank Value Solution 2, sealed and shaken. Only 50 ml disposable digestion vessels (DigiTube®) manufactured by SPC-Science were used for the complete validation. These vessels fulfil the requirements of ASTM class 'A' with regard to accuracy of volume.

Tab. 6 Sample composition of the quality control samples for determination of the recovery

Platinum in the QC samples	Number	Spiking Solution 1	Spiking Solution 2
[mg]		[µl]	[µl]
0.12	6	12	–
1.20	6	–	60
2.40	6	–	120

The autosampler was used to dilute all the samples (spiked filters and quality control samples) by a factor of 50 and then they were analysed in accordance with Section 7. The results for the conversion rate and recovery with reproducibility are shown in Table 7.

Tab. 7 Conversion rate and recovery with reproducibility

Spiked platinum per filter	Conversion rate	Recovery	Reproducibility
[mg]	[%]	[%]	[%]
0.12	98	99	4.3
1.20	98	95	1.5
2.40	96	91	0.9

The platinum concentration in air is calculated using the mean recovery rate of 95%.

10.3 Expanded uncertainty of the entire method

The expanded uncertainty is obtained by estimation of all the relevant influencing parameters ('bottom-up' method). The uncertainty of the entire method and thus also of the analytical result consists principally of the uncertainty contributions of sampling, a combination of the air sample volume and the sampling device (sampling effectiveness) according to Appendix C in DIN EN ISO 21832 (DIN 2020), the volume of the prepared sample solution, the dilution, the recovery, storage and the influences on the measurement values, in particular the scatter of the calibration function and the laboratory's own reproducibility (precision).

Table 8 summarises all the determined uncertainty contributions for the three concentrations investigated.

Based on a sampling period of 120 minutes and a flow rate of 10 l/min (GSP) a combined uncertainty of 9.31% is obtained for sampling of the inhalable particle fraction with transport and storage.

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

Tab. 8 Determination of the expanded concentration-dependent uncertainty u using the bottom-up method

	2 × OELV	1 × OELV	0.1 × OELV
Platinum concentration of the measurement solution [mg/l][a)]	0.960	0.480	0.048
Platinum concentration in the air [mg/m³]	2	1	0.1
Uncertainty of sampling, transport and storage us [%]		9.31	
Uncertainty associated with the recovery, uab [%]	3.4	3.4	7.6
Uncertainty associated with the analytical variability, uav [%]		7.8	
Expanded uncertainty, u [%]	25.2	25.2	28.7

a) Concentration after dilution of the measurement solution by a factor of 50 using the autosampler

10.4 Limit of quantification

As the filters exhibited no platinum blank values, the absolute limit of quantification was determined as stipulated in DIN 32645 (DIN 2008) according to the calibration line method from an equidistant 10-point calibration in the lower concentration range of 5.0 to 50 µg/l of platinum. Two platinum stock solutions with concentrations of 100 µg/l (A) and 10 µg/l (B) were prepared for this purpose and diluted using the autosampler according to the following specifications in Table 9 to yield the ten calibration standards.

The calibration standards and the blank value solutions are analysed under the AAS operating conditions described in Section 6 and a linear calibration function is plotted.

Tab. 9 Calibration standards for external calibration to determine the limit of quantification

Calibration solutions	Platinum stock solution	Concentration [µg of platinum/l]	Volume of Blank Value Solution 1 [µl]	Volume of platinum stock solution [µl]
Pt blank value		0	20	0
Pt Standard 1	B	5	10	10
Pt Standard 2	B	10	0	20
Pt Standard 3	A	15	17	3
Pt Standard 4	A	20	16	4
Pt Standard 5	A	25	15	5
Pt Standard 6	A	30	14	6
Pt Standard 7	A	35	13	7
Pt Standard 8	A	40	12	8
Pt Standard 9	A	45	11	9
Pt Standard 10	A	50	10	10

The limit of quantification is 15 µg/l. From this, a relative limit of quantification of 31.3 µg/m³ is obtained for an air sample volume of 1.2 m³, a digestion volume of 50 ml and a sample dilution factor of 50. For a sampling period of 15 minutes under the same conditions this is equivalent to 250 µg/m³.

If the OELV is further lowered, the sensitivity of the method ensures that 0.75 µg Pt/filter and 0.63 µg Pt/m³ can actually be determined without dilution for an air sample volume of 1.2 m³ and a digestion volume of 50 ml in the case of the established limit of quantification of 15 µg/l.

10.5 Storage stability

Storage stability was checked by spiking three independent quartz fibre filters with 0.12 mg, 1.2 mg and 2.4 mg of platinum, respectively, in accordance with Section 10.2 and Table 5. The filters were stored at room temperature for < 4 hours, 1 week, 2 weeks, 3 weeks and 4 weeks in the desiccator, then prepared and analysed in accordance with Section 5.

After a storage period of 4 weeks at room temperature the mean recoveries of 98.4%, 94.7% and 94.3% for platinum were determined for the filter deposits of 0.12 mg, 1.2 mg and 2.4 mg. Therefore, the loaded filters are stable at room temperature in the desiccator for four weeks.

10.6 Selectivity

The selectivity of the method depends largely on the selection of the wavelength and thus on spectral interferences.

Spectral interferences are caused by emission lines from interferents and molecules in the sample matrix.

Neither matrix effects nor non-spectral interferences were observed due to the high dilution of the sample solution by a factor of 50 and due to the use of background compensation by means of Zeeman correction.

Possible – in the case of different sample compositions – occurring matrix effects can be taken into account by application of the standard addition method, if necessary.

10.7 Comparison with an open digestion method

The high-pressure microwave digestion method described here was compared with an open digestion method in the DigiPREP MS graphite heating block. For this purpose, the same digestion matrix (3 ml of nitric acid 65% and 9 ml of hydrochloric acid 30%) and two digestion solutions with different concentrations (24 mg Pt/l and 48 mg Pt/l) were used in the same manner as for the high-pressure microwave digestion.

The open acid digestion was carried out as stipulated in the temperature program described in Section 4.3. The results in Table 10 show that the results of both the digestion methods are similar.

Tab. 10 Comparision of the two digestion methods

	Open digestion method		High-pressure microwave digestion	
	Recovery [%]	Relative standard deviation [%]	Recovery [%]	Relative standard deviation [%]
Platinum concentration of the digestion solution 24 mg/l	99	0.9	98	1.2
Platinum concentration of the digestion solution 48 mg/l	96	1.5	98	0.6

11 Discussion

Platinum can be determined in workplace air in a concentration range of a tenth up to twice the currently valid OELV of 1 mg/m³ (inhalable particle fraction) with the analytical method described here. The analytical method is also suitable for checking an excursion of the OELV by a factor of eight for 15 minutes.

If the OELV is further lowered, the sensitivity of the method ensures that 0.75 µg Pt/filter and 0.63 µg Pt/m^3 can actually be determined without dilution for an air sample volume of 1.2 m^3 and a digestion volume of 50 ml in the case of the established limit of quantification of 15 µg/l (see Section 10.4).

Alternatively, it is possible to use a membrane filter, e. g. nitrocellulose.

All filter batches should be checked before use.

In the case of a large sample loads excessive wear and tear of the graphite furnace has been observed, therefore the graphite furnace should be replaced regularly.

Notes

Competing interests

The established rules and measures of the Commission to avoid conflicts of interest (www.dfg.de/mak/conflicts_interest) ensure that the content and conclusions of the publication are strictly science-based.

References

AGS (Ausschuss für Gefahrstoffe) (2016) Technical rules for hazardous substances (TRGS 402). Identification and assessment of the risks from activities involving hazardous substances: inhalation exposure [TRGS 402 in German language, 2016]. Dortmund: BAuA. https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-402.pdf?__blob=publicationFile&v=4, accessed 31 Mar 2021

AGS (Ausschuss für Gefahrstoffe) (2021) Technische Regeln für Gefahrstoffe (TRGS 900). Arbeitsplatzgrenzwerte. Dortmund: BAuA. https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-900.pdf?__blob=publicationFile&v=18, accessed 31 Mar 2021

DIN (Deutsches Institut für Normung), editor (2008) DIN 32645:2008-11. Chemische Analytik – Nachweis-, Erfassungs- und Bestimmungsgrenze unter Wiederholbedingungen – Begriffe, Verfahren, Auswertung. Berlin: Beuth. https://doi.org/10.31030/1465413

DIN (Deutsches Institut für Normung), editor (2014) DIN EN ISO 13137:2014-03. Workplace atmospheres – Pumps for personal sampling of chemical and biological agents – Requirements and test methods (ISO 13137:2013); English translation of German version EN ISO 13137:2013. Berlin: Beuth. https://doi.org/10.31030/2024922

DIN (Deutsches Institut für Normung), editor (2020) DIN EN ISO 21832:2020-08. Workplace air – Metals and metalloids in airborne particles – Requirements for evaluation of measuring procedures (ISO 21832:2018); English translation of German version EN ISO 21832:2020. Berlin: Beuth. https://doi.org/10.31030/3157765

DIN (Deutsches Institut für Normung), editor (2021) DIN EN 482:2021-05. Workplace exposure – Procedures for the determination of the concentration of chemical agents – Basic performance requirements; English translation of German version EN 482:2021. Berlin: Beuth. https://doi.org/10.31030/3211072

Statista Research Department (2022) Minenproduktion von Platin nach den wichtigsten Ländern in den Jahren 2020 und 2021. https://de.statista.com/statistik/daten/studie/194141/umfrage/minenproduktion-von-platin-nach-laendern/, accessed 11 Apr 2022