

Manganese – Determination of manganese and its inorganic compounds in workplace air using atomic absorption spectrometry (AAS)

Air Monitoring Method – Translation of the German version from 2021

Keywords

manganese; hazardous substances; air analyses; workplace measurement; furnace atomic absorption spectrometer; GF-AAS; acid digestion; high-pressure microwave digestion; quartz fiber filter

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Abstract

The analytical method described here permits the simultaneous determination of manganese dusts and manganese compounds occurring in particulate form in the workplace air in a concentration range of one tenth up to twice the currently valid German Occupational Exposure Limits of 0.2 mg/m³ (inhalable dust fraction) and 0.02 mg/m³ (respirable dust fraction). The peak limits, each with an excursion factor of 8, can also be checked.

Sampling is carried out using a flow-regulated pump to draw a defined volume of air through a quartz fibre filter. The sampling head predetermines whether the inhalable fraction or respirable fraction is collected. Intake cones for 10 l/min as well as for 3.5 l/min can be used. The manganese deposited on the filter in the form of dust and particles is 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. If matrix influences occur, then the standard addition method is used for quantitative evaluation. The limit of quantification is 13.6 pg absolute and 0.02 µg/m³ for a sampling volume of 1.2 l and a sampling period of 2 h. The mean recovery is 96% and the expanded uncertainty for the validation range of 0.002 to 3.2 mg/m³ is 30% for the inhalable fraction and 27% for the respirable fraction.

Method number	1
Application	Air analysis
Analytical principle	Atomic absorption spectroscopy (AAS)

1 Characteristics of the method

Repeatability:	Standard deviation (rel.): at a concentration of 9.6 µg/l	$s = 3.7\%$
Reproducibility:	Standard deviation (rel.): at a concentration of 24 µg/filter or 100 µg/filter	$s = 1.1\text{--}6.7\%$
Expanded uncertainty:	30% for the inhalable fraction 27% for the respirable fraction in the concentration range from 0.002 to 3.2 mg/m ³	
Limit of quantification:	13.6 pg (0.68 µg/l sample solution) absolute 0.00002 mg/m ³ for an air sample volume of 1200 l and a sampling period of 2 h 0.00004 mg/m ³ for an air sample volume of 420 l and a sampling period of 2 h 0.00012 mg/m ³ for an air sample volume of 150 l and a sampling period of 15 minutes	
Recovery:	$\eta = 0.96$ (for 24 µg/filter) and 1.0 (for 100 µg/filter)	
Sampling recommendations:	Sampling period:	2 h
	Air sample volume:	1200 l, alternatively 420 l
	Flow rate:	10 l/min, alternatively 3.5 l/min
	For short-term measurements:	15 min; 150 l

2 Description of the substances

Manganese [7439-96-5]

The Occupational Exposure Limits (OEL) for manganese and its inorganic compounds are 0.2 mg/m³ (inhalable dust fraction) and 0.02 mg/m³ (respirable dust fraction); the short-term exposure limits are assigned to Peak Limitation Category II with an excursion factor of 8 (AGS 2021). In the list of MAK and BAT values, the MAK values for manganese and its inorganic compounds are the same as the Occupational Exposure Limits (DFG 2019). Detailed information on the toxicity of manganese and its inorganic compounds can be found in the MAK value documentation (Hartwig 2015).

3 General principles

The analytical method permits the simultaneous determination of manganese dusts and manganese compounds occurring in particulate form in the workplace air in a concentration range of one tenth up to twice the currently valid Occupational Exposure Limit (OEL) of 0.2 mg/m³ (inhalable dust fraction) and 0.02 mg/m³ (respirable dust fraction) (AGS 2021). The peak limits, each with an excursion factor of 8, can also be checked (AGS 2021; DIN 2015).

Sampling is performed using a flow-regulated pump to draw a defined volume of air through a quartz fibre filter. The sampling head predetermines whether the inhalable fraction or respirable fraction is collected. Intake cones for 10 l/min as well as for 3.5 l/min can be used. The manganese deposited on the filter in the form of dust and particles is 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. If matrix influences occur, then the standard addition method is used for quantitative evaluation.

4 Equipment, chemicals and solutions

4.1 Equipment

For sampling:

- Pump for personal air sampling, flow rates of 3.5 to 10.0 l/min (e.g. SG10-2, from GSA Gesellschaft für Schadstoffanalytik mbH, 40880 Ratingen, Germany)
- Personal sampling system for hazardous substances (PGP) with a sampling head for the inhalable fraction (GSP) and the respirable fraction (FSP) with an intake cone for 10 l/min or also 3.5 l/min, supplied by DEHA Haan & Wittmer GmbH, 71296 Heimsheim, Germany
- Filter cassettes for the PGP sampling system with metal support screen, supplied by DEHA Haan & Wittmer, 71296 Heimsheim, Germany
- Quartz fibre filters, diameter 37 mm, (e.g. QM-A from Whatman, VWR International GmbH, 64295 Darmstadt, Germany)

For sample preparation and analysis:

- High-pressure microwave digestion system, (e.g. MarsXpress, from CEM, 47475 Kamp-Lintford, Germany) with digestion vessels and seals made of PTFE
- Atomic absorption spectrometer with graphite furnace and autosampler (e.g. PerkinElmer PinAAcle 900Z, from PerkinElmer LAS, 63110 Rodgau, Germany)
- Manganese hollow cathode lamp (e.g. from Perkin-Elmer LAS, 63110 Rodgau, Germany)
- Adjustable piston pipette (e.g. Multipette pro 1 µl to 10 ml, from Eppendorf, 22366 Hamburg, Germany)
- Rotameter flow meter, (e.g. Influx 1 to 13 litres, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany)
- Analytical balance
- Membrane filter made of regenerated cellulose, pore width 0.45 µm, diameter 30 mm, (e.g. from Roth GmbH & Co. KG, 76185 Karlsruhe, Germany)
- Disposable syringes, 5 ml, made of polyethylene
- Volumetric flasks, 10, 25 and 50 ml, made of Duran glass
- Wide-necked flasks, 50 ml, made of polyethylene
- Plastic tweezers
- Glass funnel (e.g. diameter 55 mm)
- Autosampler vials made of polyethylene

4.2 Chemicals

- Manganese ICP standard 1000 mg/l, traceable to SRM from NIST, from Merck, 64293 Darmstadt, Germany, Order No. 1.70332
- Multi-element Standard Solution 4 for ICP, from Merck, Darmstadt, Germany, Order No. 51844
- Nitric acid (65%), Suprapur[®], from Merck, Darmstadt, Germany, Order No. 1.00441
- Hydrochloric acid (30%), Suprapur[®], from Merck, Darmstadt, Germany, Order No. 1.00318
- Palladium (10 g/l) matrix modifier for the graphite furnace-AAS, from Merck, Darmstadt, Germany, Order No. 107289
- Magnesium nitrate hexahydrate $\text{Mg}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$, Suprapur[®], from Merck, Darmstadt, Germany, Order No. 1.05855
- Tracepur[®] water, from Merck, Darmstadt, Germany, Order No. 1.00318
- Argon 5.0

4.3 Solutions

Before use, all glassware must be rinsed with dilute nitric acid (approximately 20%) and Tracepur[®] water to remove any traces of metal.

Modification solution: (1 g palladium and 0.6 g magnesium nitrate/l)

Tracepur[®] water is placed into a 25 ml volumetric flask, approx. 26 mg of magnesium nitrate hexahydrate are weighed and transferred into the volumetric flask. Additionally, 2.5 ml of palladium matrix modifier are pipetted into the volumetric flask, which is filled to the mark with Tracepur[®] water, sealed and shaken.

Manganese solution 3 for validation: (400 µg/ml)

4 ml of the manganese ICP standard (1000 mg/l) are pipetted into a 10 ml volumetric flask. Then the flask is filled to the mark with Tracepur[®] water, sealed and shaken.

4.4 Calibration standards

The calibration standards are prepared by dilution of the manganese ICP standard (1000 mg/l) as follows:

Manganese solution 1: 12.5 mg/l

0.625 ml of the manganese ICP standard is pipetted into a 50 ml volumetric flask into which approx. 30 ml of Tracepur[®] water have been previously placed. Then the flask is filled to the mark with Tracepur[®] water, sealed and shaken.

Manganese solution 2: 0.625 mg/l

1.25 ml of Manganese solution 1 is pipetted into a 25 ml volumetric flask into which approx. 20 ml of Tracepur[®] water have been previously placed. Then the flask is filled to the mark with Tracepur[®] water, sealed and shaken.

Manganese calibration solution: 12.5 µg/l

0.25 ml of nitric acid (65%) and 0.5 ml of Manganese solution 2 are pipetted into a 25 ml volumetric flask into which approx. 20 ml of Tracepur[®] water have been previously placed. Then the flask is filled to the mark with Tracepur[®] water, sealed and shaken.

Blank value solution:

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

Calibration standards:

The six calibration standards are prepared using the autosampler from the manganese calibration solution and the blank value solution according to the following specifications.

Tab. 1 Pipetting scheme for the preparation of the six calibration solutions

	Concentration [µg of manganese/l]	Volume of blank value solution [µl]	Volume of manganese calibration solution [µl]
Manganese blank value	0	25	0
Manganese Standard 1	1.25	23	2
Manganese Standard 2	2.5	21	4
Manganese Standard 3	5	17	8
Manganese Standard 4	7.5	13	12
Manganese Standard 5	10	9	16
Manganese Standard 6	12.5	5	20

Control solution: 10 µg/l

0.25 ml of nitric acid (65%) and 0.25 ml of Multi-element Standard Solution 4 are pipetted into a 25 ml volumetric flask into which approx. 20 ml of Tracepur® water have been previously placed. Then the flask is filled to the mark with Tracepur® water, sealed and shaken.

5 Sampling and sample preparation

5.1 Sampling

At the beginning of sampling a quartz fibre filter is inserted into the GSP or FSP sampling head (Riediger 2001; Siekmann 1998). If an intake cone for 10 l/min is used then the filter must be fitted with a support screen. Preferably, a flow rate of 10 l/min is set using a flow-regulated pump and the intake cone designated for the purpose is fitted. Alternatively, an intake cone suitable for a flow rate of 3.5 l/min can also be used. Sampling periods of 15 minutes (monitoring the peak limit) and two hours can be selected. At a sampling time of 2 hours this corresponds to an air sample volume of 1200 litres or 420 litres, for a sampling period of 15 minutes it is 150 litres.

After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ±5%, it is advisable to repeat the measurement (DIN 2014). The filter cassette with the loaded filter is sealed with the caps designated for the purpose and transported to the laboratory for analysis. The air samples are stored at room temperature until analysis.

One blank sample (field blank) per sample series must be prepared. This differs from the analytical sample in that no sample air was drawn through the filter. This blank sample is then stored and prepared in the same manner as the other samples.

5.2 Sample preparation

The loaded filter is carefully removed from the filter cassette using tweezers, placed into a digestion vessel and 6 ml of nitric acid (65%) and 3 ml of hydrochloric acid (30%) are added.

The digestion vessel is covered with the lid and sealed with the screw-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 800 W within a period of 10 minutes and maintaining it at this level for 10 minutes. The maximum permissible control temperature is around 210°C. After the samples have been digested, they are left to cool in the microwave device. In this case, the quartz fibre filter is not digested without trace.

A pre-rinsed glass funnel is used to quantitatively transfer the digestion solution with Tracepur® water into a 25 ml volumetric flask. The volumetric flask is filled to the mark, sealed and shaken. The sample solution is transferred into a wide-necked flask and stored at room temperature until analysis. If precipitation occurs or there are non-soluble components then the sample solution is filtered through a disposable syringe using a syringe filter. Immediately before analysis, part of the sample solution is transferred into an autosampler vial.

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

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

6 AAS operating conditions

Apparatus:	PinAAcle 900Z atomic absorption spectrometer with graphite furnace with Zeemann background compensation and transversely heated graphite tube including a L'vov platform, manganese hollow cathode lamp, from PerkinElmer
Measured wavelength:	279.48 nm
Spectral slit width:	0.2 nm
Signal evaluation mode:	Peak area
Injection volume:	20 µl of sample solution or calibration standard + 5 µl of modification solution + 5 µl of blank value solution
Inert gas:	Argon (5.0)

Before the measurement commences, the device must be switched on for at least 15 minutes to allow the lamp to warm up. The temperature/time programme of the graphite tube is shown in [Table 2](#).

Tab. 2 Temperature/time programme

Program step	Furnace temperature [°C]	Temperature ramp time [s]	Dwell time [s]	Inert gas flow rate [ml/min]
1 Drying	120	1	30	250
2 Drying	140	20	40	250
3 Pyrolysis	1200	10	20	250
4 Atomisation	2200	0	3	0
5 Final heating	2450	1	3	250

7 Analytical determination

The samples prepared according to [Section 5.2](#) and the field blank value as well as a reagent blank value, consisting of nitric acid (65%) and hydrochloric acid (30%) at a ratio of 2:1 (analogous to the samples), the blank value solution and, if necessary, a filter batch blank value are analysed by means of AAS. For this purpose, 20 µl each of the solution to be investigated with 5 µl of blank value solution and 5 µl of modification solution are injected into the AAS by the autosampler and analysed according to the AAS operating conditions listed in [Table 2](#). Each sample is analysed in duplicate and the mean value is used for calculating the result.

If the manganese concentrations are above the calibration curve, the sample solutions are diluted with water and nitric acid (65%), to such an extent that for stabilisation purposes there is an acid level of at least 0.65% in the dilution (measurement solution). The appropriate dilution factor can be estimated by carrying out preliminary experiments.

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

The control solution is analysed before analysis of the sample solution and at the end of the sequence. The concentration must fall within defined limits ($\pm 10\%$), otherwise the calibration must be checked and the analysis of the sample solutions must be repeated. Thus, the stability of the analytical devices and the accuracy of the results are checked. In the case of larger series of samples, it is advisable to carry out further periodic measurements of the control solution.

A possible matrix influence must be checked at least once per sample series. For this purpose, at least one sample is analysed anew and 5 µl of the blank value solution is replaced by 5 µl of the manganese calibration solution. The recovery rate is calculated from the manganese concentration of the spiked sample after deduction of the manganese concentration of the original sample with respect to the spiked manganese amount (3.125 µg). This must be between 90 and 110%, otherwise a matrix effect must be assumed. In this case it is important to ensure that the spiked sample is within the calibration curve. If the matrix of the sample has a significant influence, the standard addition method with the sample solution or measurement solution must be used for evaluation.

8 Calibration

External calibration:

The calibration must be performed every working day. The calibration standards including the blank value prepared by the autosampler as described in [Table 1](#) are analysed to obtain the calibration function. The standards are analysed in duplicate in the same manner as the samples. The calibration graph is plotted automatically by the evaluation program of the AAS device by means of linear regression.

The control solution is analysed in order to check the calibration function.

Standard addition calibration:

In order to eliminate any possible matrix effect, the sample must undergo a standard addition calibration. The manganese concentration of the sample should be between 5 and 12.5 µg/l. The calibration standards are obtained by addition of the different amounts of manganese calibration solution to the sample according to [Table 3](#). The autosampler adds 5 µl of the modification solution to each standard and each sample solution using a pipette in the same manner as the external calibration. All standards and solutions are analysed twice and the mean value is used to calculate the result. The AAS operating conditions remain unaltered. The value of the intercept of the calibration curve with the x-axis is equivalent to the manganese concentration of the sample solution.

Tab. 3 Pipetting scheme for preparation of the standard addition calibration standards

	Spiked concentration [µg of manganese/l]	Volume of blank value solution [µl]	Volume of sample solution [µl]	Volume of manganese calibration solution [µl]
Manganese blank value	0	25	0	0
Sample		15	10	0
Manganese standard 1	5.0	11	10	4
Manganese standard 2	8.75	8	10	7
Manganese standard 3	12.5	5	10	10

9 Calculation of the analytical result

The concentration of manganese in the measurement solution is calculated by the evaluation program from the linear calibration function. The concentration of manganese 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 manganese in the workplace air is calculated according to [Equation 1](#) as follows:

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

where:

- ρ is the mass concentration of manganese in the air sample in mg/m³
- C is the concentration of manganese in the measured solution (mean value) in µg/l
- C_{blank} is the concentration of the field blank value (mean value) in µg/l
- f_D is the dilution factor
- V is the volume of the sample solution in l (here 25 ml)
- 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 2015), DIN EN ISO 21832 (DIN 2020) and DIN 32645 (DIN 2008).

10.1 Repeatability

The repeatability was determined by analysing one diluted standard solution and one diluted prepared sample solution with a concentration of 9.6 µg/l each day over a period of six days. The relative standard deviations thus obtained were 1.6% for the standard solution and 3.7% for the sample solution.

10.2 Recovery and reproducibility

For this purpose, twelve filters were each spiked with 60 µl of Manganese solution 3 (400 µg/ml for the validation). Six filters were prepared according to [Section 5.2](#). 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.

In order to obtain reference values, a pipette was used to add 60 µl of Manganese solution 3 each into six 25 ml volumetric flasks, into which Tracepur[®] water and 0.25 ml of nitric acid (65%) had been previously placed. The volumetric flasks were filled to the mark with Tracepur[®] water, sealed and shaken.

The reference values, filters for the determination of the conversion rate (without air samples) and the filters with samples for the determination of the recovery rate were diluted by a factor of 100 and analysed according to [Section 5](#). The results of the conversion and recovery rates including the reproducibility are shown in [Table 4](#).

Tab. 4 Conversion and recovery rates including the reproducibility in %

Spiked manganese per filter [µg]	Conversion rate [%]	Recovery rate [%]	Reproducibility [%]
24	100	96	1.1

Recovery with a high manganese concentration (100 µg of manganese per filter):

For this purpose, twelve filters were each spiked with 100 µl of manganese ICP Standard (1000 mg/l). Laboratory air was drawn through six filters over a time period of 2 hours at a flow rate of 3.5 l/min. All filters were prepared according to [Section 5.2](#). The reference values were prepared in the same manner as those for the recovery at low concentrations, however, 100 µl of the manganese ICP standard solution were used.

The reference values, filters for the determination of the conversion rate (without air samples) and the filters with samples for the determination of the recovery rate were diluted by a factor of 400 and analysed according to [Section 5](#). The results of the conversion and recovery rates including the reproducibility are shown in [Table 5](#).

Tab. 5 Conversion and recovery rates including the reproducibility in % at high concentrations

Spiked manganese per filter [µg]	Conversion rate [%]	Recovery rate [%]	Reproducibility [%]
100	100	100	6.7

The manganese concentration in air is calculated at a recovery rate of 96%.

10.3 Expanded uncertainty of the entire procedure

The 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 rate, the storage and the influences on the measurement values, in particular the scatter of the calibration function and the laboratory's own reproducibility (precision).

[Table 6](#) summarises all the determined uncertainty contributions, whereby there is partial differentiation between high (12 µg Mn/l) and medium concentration (6 µg Mn/l). For the uncertainty a distinction is made between not just the inhalable and the respirable fraction but also the sampling periods of 120 and 15 minutes.

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 procedure is obtained by multiplication with a probability factor ($k = 2$ for 95% confidence level).

Tab. 6 Determination of the uncertainty (u) using the bottom-up method in %

	Sampling period of 120 minutes		Sampling period of 15 minutes	
	GSP 3.5 l/min	FSP 10 l/min	GSP 10 l/min	FSP 10 l/min
u for sampling	9.1	11.7	9.4	11.8
u for the volume of the sample solution	0.1	0.1	0.1	0.1
u for dilution	1.1	1.8	1.1	1.8
u for recovery + storage	10.1	3.4	10.1	3.4
u for a measurement value at a high concentration	4.5	4.5	4.5	5.6
u for a measurement value at a medium concentration	5.6	5.6	4.5	5.6
u for a combined high concentration	14.4	13.1	14.6	13.3
u for a combined medium concentration	14.8	13.5	15.0	13.7
U for an expanded high concentration	29	26	29	27
U for an expanded medium concentration	30	27	30	27

The high concentration for a sampling period of 120 minutes, a flow rate of 3.5 l/min and a dilution factor of 400 is equivalent to a concentration of 0.30 mg/m³ of manganese in air. For a sampling period of 120 minutes, a flow rate of 10 l/min and a dilution factor of 100 the high manganese concentration of the measurement solution is equivalent to a concentration of 0.026 mg/m³ of manganese in air.

For a sampling period of 15 minutes, a flow rate of 10 l/min and a dilution factor of 100 the high manganese concentration of the measurement solution is equivalent to a concentration of 0.21 mg/m³ of manganese in air.

10.4 Limit of quantification

As part of the development of the method, the limit of quantification was determined in accordance with DIN 32645 (DIN 2008) using the blank value method based on six analysed filter blank values from two batches. This was equivalent to 0.68 µg/l of manganese.

The relative limits of quantification were 0.000015 mg/m³ for an air sample volume of 1200 litres, 0.000040 mg/m³ for an air sample volume of 420 litres and 0.00012 mg/m³ for an air sample volume of 150 litres.

Note: The limit of quantification determined according to the calibration line method (in the concentration range of the calibration standards between 1.25 and 12.5 µg/l) at 0.66 µg/l is comparable to the absolute limit of quantification obtained using the blank value method.

10.5 Storage stability

Eight filters were each spiked with 24 µg of manganese as described for determination of the recovery in Section 10.2. The filters were stored for 21 days in the filter cassettes at room temperature, then prepared, diluted and analysed. The losses during storage were 8%. Hence, storage stability of the quartz fibre filter over a time period of three weeks at room temperature is ensured.

The storage stability of loaded membrane filters over a time period of more than 4 weeks is ensured and should also apply to quartz fibre filters.

Additionally, two prepared, diluted sample solutions, one from the recovery experiments and one from the storage stability experiments were reanalysed after 56 and 41 days of storage at room temperature. The solutions were both stable. Storage stability of the prepared sample solutions with a concentration of approx. 9.5 µg/l of manganese is ensured over 56 days.

10.6 Selectivity

The selectivity of the method depends largely on the selection of the wavelength and thus on spectral interference. Spectral interference is caused by emission lines from interferents and molecules in the sample matrix.

Dilution of the sample solution can reduce possible non-spectral interferences and matrix effects. Interference can also be effectively eliminated by use of the Zeemann correction. Possible matrix effects can also be eliminated by calibration of the sample solution in accordance with the standard addition method.

It is not possible to differentiate between the individual manganese compounds.

Quartz fibre filters can also be substituted by membrane filters.

11 Discussion

The analytical method described here permits the determination of manganese and inorganic manganese compounds in workplace air in a concentration range of a tenth up to twice the currently valid OEL value of 0.2 mg/m³ (inhalable dust fraction) and 0.02 mg/m³ (respirable dust fraction). The analytical method is suitable for checking compliance with the short-term value.

12 Appendix: Accuracy by means of comparative measurements and inter-laboratory comparability investigation

In 2017 – in the context of an inter-laboratory comparison (Pitzke et al. 2020), organised by the IFA and carried out by members of the “Air Analyses” working group of the DFG – the high-pressure microwave digestion described here was compared to open digestion. For this purpose, two grinding dusts were weighed, prepared and analysed. The manganese concentrations of the dusts for open digestion were 0.20% and 2.4% of the mass on average with relative standard deviations of 5.6% and 2.4% for six participating laboratories. Concentrations of 0.26% and 0.22% were determined with the analytical method described here. Comparability between the high-pressure microwave digestion described here and open digestion is thus shown.

In 2013 and 2015 two filters loaded with metal were examined in the context of an inter-laboratory comparison carried out by Sigma-Aldrich (RTC AIR2013-2 and AIR2015-2). The loaded manganese amounts were 87 and 156 µg. The measured concentrations were 82 and 143 µg. The required z-score of less than 2 was then achieved by a margin of 0.7 and 0.8 and the inter-laboratory comparison was passed. Thus, the accuracy of the method has been confirmed.

Notes

Competing interests

The established rules and measures of the commission to avoid conflicts of interest (https://www.dfg.de/en/dfg_profile/statutory_bodies/senate/health_hazards/conflicts_interest/index.html) ensure that the content and conclusions of the publication are strictly science-based.

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